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PRESIDENT'S LETTER

The advent of molecular photochemistry and photophysics. When was that? Difficult to say, but nobody will argue that the following scientists were not tightly associated to it: Michael Kasha, Howard E. Zimmerman, Nicholas J. Turro, Ralph S. Becker. Great scientists who left their marks on our field, and who all passed away in the past months, Kasha only a few days before I have started to write this letter.

Clearly, I am from a different generation. But I had the privilege to still meet and get to know some of them, even if transiently, at conferences and on other occasions, and it is now time to recollect these memories. In 2001, Howard Zimmerman had invited me to take up a visiting professorship at the University of Wisconsin, and I had the joy every Thursday of the week to have lunch just with him and learn from him for an entire semester. Turro I knew from his famous book when I did the first photochemical experiments during my studies. My respect was then sufficient to ask him in 1994 to put a small dedication in his very book for me. Although I lost later much of my initial respect for the eminent figures in the field – at the end of the day we are all just regular scientists, and especially Turro was easy to talk to, we had many discussions at conferences and I visited his lab at Columbia – I am now happy to have his dedication in my "Turro", the old one I should say since a new edition has finally come out a couple of years ago. You can read his obituary in this Newsletter, along with that of Ralph S. Becker.

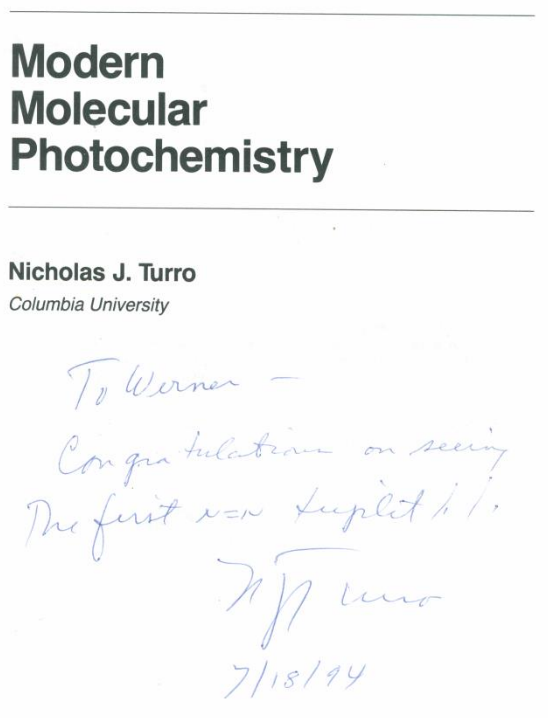
I even can report on an encounter with Mike Kasha, "already" in 1993, 20 years ago. It was at my first photochemistry conference, the XVIth International Conference on Photochemistry held in Vancouver. Actually, at this conference I decided to enter academia, and not industry. I think I must have been extremely lucky back then that I got selected – as a rather fresh PhD student with Waldemar Adam – to give a talk at an international conference. So far so good, but it came worse – or better. My short talk (by the way on "Substituent Effects on Intersystem Crossing in Localized Triplet Biradicals" was scheduled in one of the very few plenary sessions –

right before the big Kasha, the Kasha´s rule Kasha, whom I had not expected to be active any more. This guaranteed me the largest possible audience, of course: All came to see Mike Kasha, but, before, they had to listen to me. I actually do not remember exactly what Kasha´s talk was about. But what I do remember is that he built up a lot of tension about a spectroscopic research project, and when everybody was expecting the decisive experiment to be unveiled, he shocked the audience by saying that this project had to be stopped because the involved PhD student had been gunned down in the streets of Miami. Some in the audience laughed, others found it inappropriate. Clearly a good way to get attention. Then Kasha soberly turned to another project in his plenary lecture. I am not sure whether this described his character (we hope to publish an obituary in our next Newsletter), but that is what I remember of my first encounter with him. Needless to say, I never gave a talk right before Kasha ever again, in retrospect the sequence of talks appears anyways as a trivial coincidence, but at that time, as a young student with an emerging interest in photochemistry, I took it as a major distinction.

Fortunately, the field of photochemistry is not only about the past, although we have a feature article on the history of EPA reprinted in this Newsletter as well. We also feature some exciting science and the International Conference on Photochemistry 2013 in Leuven is just ahead. EPA is alive and kicking, we are just about to get a bit involved in electronic media, you may want to have a look at our recently installed Facebook page, just look for "European Photochemistry Association." And please "like" our page and subscribe to it, so we get going.

Werner Nau

Jabobs University Bremen



Modern Molecular Photochemistry

Nicholas J. Turro
Columbia University

To Werner –
Congratulations on seeing
the first N=N triplet !!
N J Turro
7/18/94

A small personal memory of Nick Turro (1938–2012). The dedication reads: “To Werner – Congratulations on seeing the first N=N triplet !! N. J. Turro 7/18/94”

OBITUARY

Nicholas J. (Nick) Turro (1938 - 2012)

Nicholas J. (Nick) Turro, William P. Schweitzer Professor of Chemistry at the Columbia University in the City of New York (USA) passed away on November 24, 2012 at the age of 74. He belongs to the pioneers of photochemistry in the 20th century in a congenial spirit with his PhD supervisor George S. Hammond and he became the most influential of Hammond's disciples. From the very early days of his scientific career Nick Turro was the prototype of an interdisciplinary researcher at the crossroads of various disciplines of chemistry, material science, biophysics etc. always using one common tool, i.e. the *photon as a reagent for initiating photoreactions and as a product of deactivation of electronically excited molecules*.

Nick Turro was born on May 18, 1938 in Middletown, Connecticut (USA). With a BA degree from Wesleyan University, he attended the graduate school at Cal Tech and received his PhD degree with George S. Hammond in 1963. Following a postdoctoral year at Harvard with Paul D. Bartlett, he joined the faculty at Columbia University already in 1964 as an instructor of chemistry and was promoted to full professor at the age of 31 as one of the youngest professors at that time. He served the Columbia University in many substantial aspects including to be the Chair of the Chemistry Department (1981–1983) and Co-Chair of the Chemical Engineering Department (1997–2000).

Turro's group in 1977 - From left to right in a circle: Secretary Sandy, next person (not known), William R. Cherry, Manfred Mirbach, Kuo-Chang Liu, Vaidhyanathan Ramamurthy (Murthy), Yoshikatsu Ito, William Farneth, A. K. Chandra, Turro, Ming-Fea Chow, and Marlis Mirbach.

In 1981 he was appointed *William P. Schweitzer Professor of Chemistry* and in 1997 *Professor of Chemical Engineering and Applied Chemistry* followed by *Professor of Earth and Environmental Engineering at the H. Krumb School of Mines, Columbia University* in 1998. With his passing part of the soul of Columbia's Chemistry has been lost, at least for his older colleagues and friends.

Turro's group on May 18, 2011 (his 73rd birthday)

In almost half a century Nick Turro published more than 950 scientific papers and he was selected as one of the most highly cited chemists for the past two decades. His research covered the fundamental principles of photochemistry, photophysics and spectroscopy and he contributed to almost all aspects of these topics, for example the classification of photoreactions (with Dauben and Salem), singlet oxygen, magnetic field and isotope effects, photoreactions in constraint media such as micelles, dendrimers, DNA etc. He is one of the pioneers of Supramolecular Photochemistry, a subdiscipline which became extremely important during the last two decades and which has a strong impact for material science as well as for life science. Turro summarized his own contributions and interests in a Perspective Article entitled *Fun with Photons, Reactive Intermediates, and Friends. Skating on the Edge of the Paradigms of Physical Organic Chemistry, Organic Supramolecular Photochemistry, and Spin Chemistry* which was published in 2011.[1] In this Perspective he presented a review and survey of the science and philosophy of his research as a physical organic chemist and photochemist. Investigations of high energy content molecules in electronically excited states and the development of electronic spin and supramolecular photochemistry are summarized as well as most recent research dealing with the nuclear spin chemistry of H_2 incarcerated in fullerenes. The role of paradigms, structure, and geometric thinking in his own cognitive and intellectual development is also discussed in this Perspective.[2-3]

Nick Turro's very creative and groundbreaking achievements in chemistry were recognized with the 2011 *Arthur C. Cope Award in Organic Chemistry*, given annually "to recognize outstanding achievement in the field of organic chemistry," and with the *2000 Willard Gibbs Award*, which recognizes "eminent chemists who...have brought to the world developments that enable everyone to live more comfortably and to understand this world better." He is also the recipient of many other awards and in 2013 was honoured posthumously with the inaugural *George S. Hammond Award* by the Inter-American Photochemical Society. Nick was elected to two of the most prestigious scientific academies, the National Academy of Sciences and the American Academy of Arts and Sciences, already at the age of 43. He authored several influential books including *Modern Molecular Photochemistry of Organic Molecules*, and was selected as one of the most highly cited chemists for the past two decades. Nick Turro was not only a brilliant scientist but also a highly regarded teacher and his teaching accomplishments were recognized by many awards, including his selection as a *Distinguished Teacher Scholar* by the National

Science Foundation (2002) and the *George C. Pimentel Award in Chemical Education* by the American Chemical Society (2004). This all together reflects his unique ability to organize complex information, seemingly unrelated to most others, from a wide range of subjects, in a very logical and retrospectively simple manner.

Characterizing Nick without mentioning Sandy, his wife for more than 50 years would be totally incomplete. For his students, postdocs, guest scientists and collaborators Sandy was the "non-scientific centre" keeping the *Turro-family* together. His own personal family always played an important role in his life. He was a warm-hearted father of two daughters and grandfather of five grandchildren leaving behind.

Nick's influence on his numerous scholars, colleagues and friends was tremendous. We lost a wonderful person.

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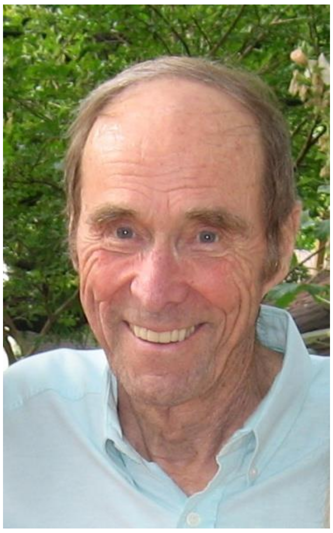
[1] N. J. Turro, *J. Org. Chem.* **2011**, *76*, 9863 – 9890
[2] N. J. Turro, *Angew. Chem. int. Ed.* **1986**, *25*, 882-901.
[3] N. J. Turro, *Angew. Chem. int. Ed.* **2000**, *39*, 2255-2259.

On May 11, 2013 the Chemistry Department of Columbia University recognized Turro's outstanding contributions and his influence on the scientific community by a memorial. A copy of the lifestream can be watched via the Webcast Portal of Columbia: http://turroserver.chem.columbia.edu/

Ralph Sherman Becker (1925-2013)



Our great friend and colleague Ralph Sherman Becker, Professor Emeritus at the University of Houston, died on February 11th, 2013. Professor Becker made a major contribution to the development of Physical Chemistry and in particular of Photophysics and Photochemistry at an international level. Our longstanding friendship and scientific collaboration and his several extended visits at the University of Perugia in Italy have induced me to pay tribute to him in this European Photochemistry Association News Letter. This will not be a traditional "obituary", but a sort of remembrance of his human touch and of the deep mark he has left in Photochemistry in

Europe and particularly in Italy. Citations of his articles appearing in this report are only those related to our scientific collaboration.

Ralph Sherman Becker was born in 1925 and grew up in northern Illinois. He served his country, during World War II, as a navigator in the 8th Air Force, flying 28 missions. He received his Bachelor's degree in Chemistry from the University of Vermont, his Master's degree from the University of New Hampshire and in 1955 he received his PhD degree from Florida State University.

Professor Becker taught at the University of Houston for 37 years and in 1978 was the first recipient of the coveted Ester Farfel Award for faculty excellence. His long and distinguished academic career spanned a wide diversity of scientific interests including chemical and biological aspects of photochemistry with attention given to potential applications of basic photochemical studies. He was a visiting professor or lecturer at universities in the USA, Canada, Central and South America, Western and Eastern Europe and Asia, including India, Japan and South Korea.

His scientific activity resulted in the many articles and books that he published which have greatly influenced thinking in Photophysics and Photochemistry. After retiring in 1992 he pursued his active devotion to scientific research through fruitful collaboration with colleagues and friends in Europe (particularly in Portugal and Italy) until just a few weeks before passing away.

He published about 200 papers which deal with photophysics, photochemistry, photochromism, molecular spectroscopy, electron attachment and model visual pigments. The book he published in 1969 on "Theory and Interpretation of Fluorescence and Phosphorescence" and a General Chemistry text in 1980 were translated into several languages.

He first came to Perugia in 1986 during a tour of visits to several photochemical laboratories in Europe. In 1988, Ugo Mazzucato , who was the head of the Photochemistry Group of Perugia, invited him to give a lecture at the Euchem Conference on Photoisomerism and Rotamerism in Assisi and in the 90s (1990 and 1999) to teach some classes to Chemistry students at the University of Perugia. The classes were to be taught by important persons in the field of international scientific research. He was the perfect teacher, not only for his renowned reputation in science but also because of his communicativeness and clarity in expressing his ideas. He attracted an audience's attention speaking not only with voice but with his whole body and especially with his hands. I remember his friendliness with students who appreciated and loved him so much because he touched them with his wit and contagious sense of humor. I always appreciated his willingness to listen to other people's opinions, he especially encouraged young students to speak their mind and he took them into great consideration. At the end of classes he liked to have *pizza* together with all the students.

Ralph was truly a master of science and life. I am fortunate to have been in touch with him for so many years not only as a scientific collaborator but also as a friend. Ralph was an enthusiastic lover of life. He was very generous in dedicating his time to people associated with him as well as being generous with his financial resources. I remember in 2009 when the city of L'Aquila, central Italy, was decimated by a killer earthquake that caused more than three hundred victims, he immediately asked me how he could help and how he could provide financial support to people hit by the disaster. In completely different circumstances, he generously offered to personally pay for a post-doc position for one of our PhD students and it was only the Italian bureaucracy that impeded him from doing it.

He loved beauty. I remember his admiration of the art and nature in Italy and his delight upon hearing the birds singing when he was in Assisi for the Euchem Conference. He was also fond of the mountains and in these last years when he learned that we had been skiing in the Dolomites, he wrote me with great regret "I envy you because I love them very much".

Also science was included in his love for life. His attitude when he had exciting scientific results reminded me of Newton's thinking about his great discoveries. He used to say: "I feel like a kid that is playing on the seashore, enjoying himself by picking up a smoother stone or a brighter shell, while the infinite ocean of truth in front of me has not yet been explored ".

Scientific collaboration of Professor Becker with the Photochemistry Group of Perugia started in the 1990s leading to numerous published articles concerning the spectroscopy, photophysics and photochemistry of different classes of organic molecules such as thienyl-ketones (*J. Phys. Chem.* ***1995****, 99, 1410*), pyrans and thiopyrans (*J. Photochem. Photobiol. A: Chem.* ***2006,*** *177, 34*), diarylethenes (*J. Photochem. Photobiol. A: Chemistry* ***1996****, 100, 57*; *J. Am. Chem. Soc.* ***1999****, 121, 1065*), and others involving also Ralph's collaborators in Portugal, concerning oligothiophenes (*Pure Appl. Chem.* ***1995,*** *67, 9*; *J. Phys. Chem.* ***1996****, 100, 18683*), coumarins (*J. Chem. Phys.* ***1997,*** *107, 6062*), oligopolyfurans (*J. Phys. Chem. A* ***2000****, 104, 6907*), furan, pyrrole, and thiophene-containing oligomers (*J. Chem. Phys.* ***2002,*** *117, 4428*), furanochromones (*Photochem. Photobiol.* ***1998****, 67, 184*), β-carbolines (*Photochem. Photobiol.* ***2005****, 81, 1195*) and flavothiones (*J. Phys. Chem. A* ***2000****, 104, 6095; Photochem. Photobiol.* ***2003****, 77, 22; Phys. Chem. Chem. Phys.* ***2003****, 5, 3469*).

Among the various subjects that Ralph treated, photochromism was one of the topics that he loved most and that he pursued throughout his long scientific career. He was fascinated by photochromic molecules with their ability to undergo light-triggered color and shape changes offering a broad array of applications. He was the first to publish on and patent (*USA* ***1971*** *Patent number 3,567, 605*) many photochromic compounds now used in some optical arrangements and to demonstrate the structure of their photoproducts through very elegant experiments (*J. Phys. Chem.* ***1967****, 71, 4045*). Some of the different classes of photochromic molecules he studied were chromenes (*J. Am. Chem. Soc.* ***1966****, 88, 5931; Photochem. Photobiol.* ***1970****, 12, 383; Photochem. Photobiol.* ***1971****, 13*, *423; J. Photochem.* ***1986****, 33, 187*), pyrans and thiopyrans (*J. Phys. Chem.* ***1968****, 72, 997*), fulgides (*J. Am. Chem. Soc.* ***1968****, 90, 3654; J. Phys. Chem.* ***1986,*** *90, 2651*), anils (*J. Am. Chem. Soc.* ***1967,*** *89, 1298; J. Chem. Phys.* ***1968,*** *49, 2092*), spiropyrans (*J. Am. Chem. Soc.* ***1970****, 92, 1289 and 129; J. Phys. Chem.* ***1986****, 90, 62; J. Photochem.* ***1986,*** *34, 83*), and dihydroquinolines (*J. Am. Chem. Soc.* ***1969****, 91, 6513; J. Chem. Soc. Perkin Trans. II* ***1972****, 17).* Properties and reactivity of the excited states of these molecules have been investigated through stationary absorption and emission spectra, time resolved transient spectroscopy, dynamic luminescence techniques and computational methods. Most of his pioneering works on this subject have received an outstanding number of citations.

I had the privilege to collaborate with Professor Becker in the field of photochromism and to publish together a number of papers dealing with kinetic-mechanistic aspects of the photochromic reaction (*Mol. Cryst. Liq. Cryst,* ***1997****, 298, 137****;*** *Photochem. Photobiol.* ***2000****, 72, 632; Chem. Phys.* ***2005****, 309, 167).* But especially our collaboration developed what became the principal target of his research in these last years, namely the "vibronic effect" which signed a sort of revolution in what was the conventional thinking about excited state relaxation mechanisms.

Professor Ralph Becker and his wife Phyllis enjoying dinner with some students and colleagues at a restaurant in the neighborhoods of Perugia (September 2003)

The story started in 1966 when Professor Becker, together with his first post-doctoral student, Josef Michl, reported that fluorescence yield of some spiropyrans unexpectedly dropped with decreasing wavelength of excitation (*J. Am. Chem. Soc.* ***1966****, 88, 5931*). Later, in

1969 (*J. Chem. Phys.* ***1969****, 50, 239*), this investigation was expanded to other molecules measuring relative fluorescence yields as a function of the vibronic quantum number excited within a singlet excited state. With only fluorescence data available, he had the great intuition that wavelength dependence of fluorescence was due to competition between vibrational relaxation and photochemistry at each vibrational level excited. For unreactive molecules, in fact, fluorescence was wavelength-independent. This was called "vibronic effect". With some co-workers he observed vibronic effect in different photochromic molecules, such as spiropyrans (*J. Am. Chem. Soc.* ***1970,*** *92, 1295*) and fulgides (*J. Am. Chem. Soc.* ***1968,*** *90, 3654*), for example. The missing link needed to confirm his idea, was to determine what did photoreaction quantum yield have to do with decreasing wavelength of excitation. An important observation for a fulgide was that the relative quantum yield of photochemistry increased with excitation to higher energy whereas that of fluorescence decreased (*J. Phys. Chem.* ***1986,*** *90, 2651*). This provided the first real proof that his intuition was well-founded.

For some years this research subject was abandoned, but was taken up again in 1999 in collaboration with the photochemistry group of Perugia. Taking advantage of instrumental improvements, it was possible to measure absolute photoreaction and fluorescence quantum yields as a function of the vibronic level excited for a naturally occurring chromene-type molecule, flindersine. As expected, based on Ralph's model, the reaction yield was found to increase with decreasing wavelength of excitation, while fluorescence decreased (*J. Am. Chem. Soc.* ***1999****, 121, 2104*). The experiments were extended to other photochromic and non-photochromic molecules, which were reactive and fluorescent or only reactive, considering also excitation in upper excited electronic states (*Photochem. Photobiol.* ***2001****, 74, 378; Chem. Phys.* ***2005,*** *316, 108; J. Phys. Chem. A* ***2005****, 109, 8684; EPA Newsletter* ***2008****, 78, 81; J. Phys. Chem. A* ***2007****, 111, 5948; Arkivoc,* ***2011****, 205*). The results in the most of cases confirmed and extended what had been found with flindersine. Such findings implied that photochemistry was as fast as vibrational relaxation and the condition for seeing the "vibronic effect" was that relaxation and reaction must be in competition at a vibrational level. This was in clear-cut contrast with traditional statements such as: "vibrational relaxation in polyatomic molecules is much faster than any other process in depopulating vibrational level". Not only the fluorescence yield and photochemistry yield depend on the specific vibrational mode and level excited but also the magnitude of the photochemical yield is largely dictated by the nature of the mode excited, not the energy of excitation. Furthermore, vibrational relaxation occurs only between levels of a given mode, without any crossing between modes. This is not at all what had been conventionally believed in the fields of photochemistry and photophysics.

Obviously such a view was not easily accepted within the scientific community of photochemists, which sometimes created difficulties for publication. As Ralph used to assert, this occurred because "a striking feature of doing research is commonly that to discover what is known in advance, in spite of the fact that the range of anticipated results is small compared to the possible results. When the outcome of a research project does not fall into this anticipated result range, it is generally considered a failure." Studies that fail to find what is expected are often not published. In fighting against what Ralph used to call "common wisdom", he liked referring to Kuhn's claims, in his book, "The price of significant scientific advance is a commitment that runs the risk of being wrong" (*T. S. Kuhn, The Structure of Scientific Revolutions, The University of Chicago Press, 1996, Chicago*): "normal science often suppresses fundamental novelties because they are necessarily subversive of its basic commitments". Ralph thought that one of the reasons why vibronic effect had not received more attention from the photochemist community was that its implications were so new to them, they were probably not sure it was correct, but in part it may also have been hard to keep track of all the new concepts.

All results and concerns on vibronic effect are collected in Ralph's last review (*J. Photochem. Photobiol. C: Photochemistry Reviews,* ***2011,*** *12, 167*) which describes, using his words, "new and unique concepts, models, mechanisms and appropriate equations not previously considered in the fields of photochemistry and photophysics". His firm belief was that they should open up new opportunities for fundamental research in photochemistry and photophysics as well as opportunities for research in applied photochemistry and photophysics.

In this note I have emphasised the human side of Ralph Becker's personality and his scientific link with the University of Perugia, which, however, represents only a minimal part of his whole scientific career, as demonstrated by the numerous publications that are not cited here. I am pleased and fortunate to have been associated with him for so many years as a colleague and a friend. There are many colleagues within the Department of Chemistry of Perugia, who join me in expressing our gratitude for having had the privilege to share a true personal friendship with him and our appreciation of his wonderful life devoted to research, teaching, family and friends.

Ralph's lovable wife often accompanied him in Italy and shared the pleasure of being with friends. We send her our heartfelt condolences. Ralph will be remembered!

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PUBLICATIONS

THE HISTORY OF THE EUROPEAN PHOTOCHEMISTRY ASSOCIATION

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Presentation – The aim of this review is to outline the history of the first four decades of the European Photochemistry Association (EPA) after its foundation in 1970. The review is divided into different sections. The first one covers the preparatory work done by leading photochemists to lay the bases for the creation of the new Association under the auspices of the Council of Europe. The second section describes the foundation of the new Association and its first three biennia of life (when the author was directly involved). The third and fourth sections summarize the progress made in the following decades and the main events that characterized the life of the Association. An Appendix illustrates in detail the history of the EPA Newsletter (with which the author collaborated until 2004). For the first period this review article is based on documentation found in the author's files and on his memory and the remaining parts are based on the reports published in the Newsletter. The pictures are taken from the EPA-Newsletter and the EPA archive with very few exceptions, as specified. It is difficult to survey the history of forty years of life of an Association without making mistakes or omissions. Many apologies to the readers for any inexactness.

1. Preliminary contacts for a new Association

The European Photochemistry Association (EPA) was founded in 1970 under the auspices of the Council of Europe. As cited in Wikipedia, "the objective of the Association is to promote the development of photochemistry in Europe and contacts among photochemists. The Association is concerned with various experimental and theoretical aspects of the interaction of light with molecular systems, ranging from basic knowledge and practical know-how in photochemistry to application in areas such as chemical synthesis, electronics, material science, nanotechnology, biology and medicine".

The preparatory work for the founding of the EPA started with some meetings of selected groups of experts in photochemistry, held in Strasbourg in 1969-1970. During the first meeting (14/15 April 1969), twelve photochemists from several European countries discussed a report prepared by Dr. Martin Fischer (BASF, Germany) and edited by the Committee for Higher Education and Research of the Council of Europe. The report dealt with the resources of photochemical research and recommended European cooperation in the field. A Working Group (WG) of five photochemists (G. Huybrechts, representing Prof. P. Goldfinger, from the Free University of Brussels, Pierre Courtot from the University of Brest, Stig Claesson from the University of Uppsala, Martin Fischer from BASF, Ludwigshafen-Rhein, and Urs Wild, representing Prof. H. Günthard, from the Federal Institute of Technology of Zürich) was established. They drafted proposals for : i) creating a scientific Association of Photochemistry under the auspices of the Council of Europe; ii) organizing informal conferences on photochemical research, based on the model of the Gordon Conferences in the USA; iii) publishing a European journal of photochemistry, and iv) increasing mobility of European researchers, particularly the exchange of PhD students.

The WG met in Strasbourg in July 1969 and in February 1970 and concluded its job with very interesting comments and proposals. It recognized the importance of photochemistry and the good level of research in the field but, in order to maintain and possibly increase the level, they recommended more substantial financial help from national governments, which at that time were inclined to give priority and significant support to more "seductive" research fields, such as molecular biology, spatial experiments, etc. As general principles for close cooperation among researchers in the field, the WG recommended stimulating contacts and exchanges among different laboratories, developing interactions between different branches of photochemistry, such as organic/physical, or related fields, such as biology, and between university and industry researchers. It was encouraged that the expenses of such interactions would be covered on a European basis. About the creation of a European Association, the WG proposed that its main aim should be to promote cooperation at the European level favouring international contacts and exchanges. They were against the creation of an international infrastructure that would put photochemical research in competition with already existing organizations, but would coordinate its efforts with them. The creation of subsidies for individual activities (short study trips, stages for PhD students and post-docs) and for group activities (seminars, summer courses, meetings to discuss specific research or teaching topics, etc.) was also recommended. Particular emphasis was given to encouraging mobility in Europe, exchanging information and developing photochemical processes in industry.

Regarding the structure of the new Association, the WG proposed a private (non-governmental) type of organization, based on individual membership and managed by the following bodies: a General Council (GC), composed of all members, to be convened once a year, a Standing Committee (SC), composed of one leading photochemist per country (to be elected by the GC), an Executive Committee (EC), composed of three members of the SC, to be elected by the GC and responsible for current decisions about grants, scholarships, etc., a Chairman, to be chosen by the GC among the members of the EC and a Secretariat. The Association would be a legally recognized, non-profit organization, possibly located in the country of the Secretariat. It was suggested that the members of the SC would invite all photochemists in their country who were joining the Association to meet and form a national section of the EPA. The organization of small research conferences was encouraged, while the publication of a European Journal was left to the discussion of the emerging organization. Detailed proposals were advanced about the increasing mobility of European photochemists. The main suggestions focussed on short-term visits to foreign laboratories, particularly for junior research workers. These were considered more important than large international meetings for the exchange of ideas.

The WG concluded its job by deciding to explore the possibilities of financing the future Association through public and private sources.

A preliminary draft of an annual budget for the Association was proposed for a total of $100,000 ($77,000 for individual activities such as grants and scholarships, $17,000 for group activities, such as contributions for workshops, summer schools, etc., and $6,000 for administration). Lastly, the WG proposed convening a meeting with leading European photochemists interested in founding the Association.

A group of leading scientists attending the third IUPAC meeting on Photochemistry (St. Moritz, July 1970) discussed all the above items further and decided to invite representatives of ten European countries to a meeting in Strasbourg to carry out the legal act of founding the European Photochemistry Association (EPA) under the auspices of the Council of Europe (Committee for Higher Education and Research). Since Prof. V. Carassiti (University of Ferrara), who had received the invitation for Italy, was unable to come, he asked the author to replace him, thus the author was fortunate to become a founding member of the Association.

2. The Foundation and first steps of the European Photochemistry Association (1970-76)

The new Association was founded at the official inaugural meeting held in Strasbourg on September 10th, 1970 with the participation of representatives (sorry for possible errors or omissions) of the following ten countries: N. Getoff (Austria), G. Huybrechts and J. Nasielski (Belgium), O. Buchardt (Denmark), P. Courtot and J. Joussot-Dubien (France), Th. Förster and A. Weller (Germany), U. Mazzucato (Italy), E. Havinga and H. J. Hagemann (Netherlands), D. Bryce-Smith (United Kingdom), S. Claesson (Sweden) and H. Labhart, Switzerland) plus an IUPAC representative (G. Quinkert). Membership in the EPA was open to anyone working in Europe in the field of photochemistry or interested in the subject. In line with the topics discussed in the preparatory meetings, the intent of the EPA was to be concerned primarily with education in photochemistry and with coordinating the activities of academic and industrial photochemists throughout Europe. It was envisioned that the EPA would arrange summer schools in photochemistry in order to bring the latest photochemical knowledge and techniques to the attention of young students as well as of people in industry and of teachers not actively engaged in the field. It was also hoped that the EPA would be able to arrange lectures by leading photochemists in European universities and research institutes with the aim of stimulating new ways of teaching and new directions of research. It was not excluded that the Association might collaborate with other bodies in organizing symposia, while excluding itself from acting as a symposium-organizing body. Subject to the availability of necessary funds, it was hoped that a number of EPA scholarships and fellowships could be created that would promote the interchange of people and exchange of ideas between European universities and research institutions. There was particular interest in making it possible for senior European photochemists to spend periods of a few weeks at those European centres where photochemical studies were not in progress and where teaching of photochemistry was comparatively neglected. Derek Bryce-Smith (University of Reading, UK) was nominated President of the EPA (Fig. 1a) and the provisional Executive and Standing Committees were appointed.

The first 1970-1972 EC was formed by the Chairman, a member (Th. Forster, Germany) (Fig. 1b), two Joint Secretaries (J. Joussot-Dubien, France, and A. E. Koerner von Gustorf, Germany) and a Treasurer (O. Buchardt, Denmark) (Fig. 1c). The first SC was formed by the members of the EC plus representatives of other countries, namely N. Getoff (Austria), E. Vander Donckt (Belgium), U. Mazzucato (Italy), E. Havinga (Netherland), H. J. Hagemann (as representative of The Netherlands industry), S. Claesson (Sweden) and H. Labhart (Switzerland).

Immediately after the Strasbourg meeting, assiduous mail contacts began among the members of the provisional committees to exchange ideas about possible activities and links with other relevant organizations and to discuss problems raised by researchers from the various countries. In the meantime, the members of the committees started making frequent contacts at the national level with the researchers and laboratories of their respective countries to disseminate information about the EPA and its aims, to encourage membership and to discuss the best way to obtain financial help for the Association from national sources (chemical societies, NRC laboratories and other foundations and research organizations).

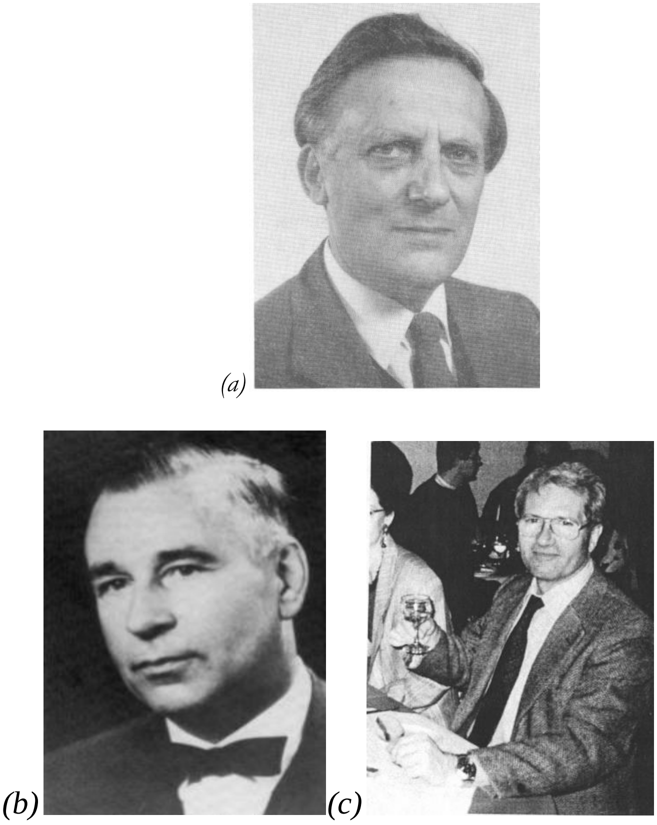

Fig. 1. Some members of the first EC 1970-72: a) Derek Bryce-Smith (Chairman) (from EPA-NL n. 42, p. 4); b) Theodor Förster (Member) (from EPA archives) and c) Ole Buchardt (Treasurer) (from EPA-NL n.52, p. 4).

In that initial period the EPA received best wishes for its activity from various chemical-related organizations and received an invitation to become a working party of the Federation of the

European Chemical Societies. It is interesting to recall that the principal role of the EPA as a precursor to a wider union of European Chemical Societies was reported in Nature (issue of December 19, 1970).

A membership fee, equivalent to about 2 £, was decided upon while membership for research groups and honorary members were envisioned. It is interesting to recall that the first outstanding photochemist to receive an honorary membership was Prof. G.O. Schenck of the Max-Planck Institut für Strahlenchemie of Mülheim, Germany (Fig. 2).

Fig. 2. Prof. Schenk, the first honorary member of the EPA. (from EPA-NL n. 19, p. 93)

It was also announced that the "Organic Chemistry of the Excited State" meeting of the Chemical Society, to be held in Reading in July 1972, would be held jointly with the EPA and that the first official scientific meeting of the Association would be held at the University of Bordeaux on the occasion of the Sixth International Conference on Photochemistry (6-8 September 1971). A meeting of the SC was also planned in order to review the progress made during the first year and discuss plans for the future. At those meetings the SC discussed ways to obtain financial support from national organizations, examined a draft of the EPA Statutes put together by O. Buchardt and E. A. Koerner von Gustorf and expressed the need to elect new official committees. Moreover, the SC suggested that the report on European photochemistry compiled by M. Fischer should be up-dated also including the Eastern European countries.

Following the Bordeaux meeting, the Council of IUPAC agreed to grant the EPA the status of an Associated Organization. The Association planned to issue an Annual World List announcing scientific meetings on photochemistry and related topics as well as workshops and other educational opportunities in the field, to be sent to all EPA members and to other interested parties. This was the germ of what would become the EPA Newsletter. In the meantime the new Association was slowly growing. A list of the members issued in March 1972 included about 80 individuals and 10 groups from 11 European countries plus 5 individuals from Israel, 5 from the USA and 1 from Canada.

In May-June 1972 the SC was renewed, based on the election of the national representatives. Voting took place in each country based on a list of candidates prepared under the supervision of the EC. Two national representatives were elected for some countries, in order to guarantee the presence of both academic and industrial photochemistry or to cover different fields of photochemistry (e.g., organic and inorganic).

The General Council of the EPA, including all the members of the Association, was convened on July 25th 1972 in Reading on the occasion of the joint Chemical Society–EPA meeting. The meeting of the GC was opened by the Chairman, Prof. D. Bryce-Smith, who gave a review of the two-year history of the EPA and described the progress made in bringing photochemists together and the efforts to support scientific and educational contacts at all levels in the field of photochemistry. It was reported that the Association had more than 200 individual members and the financial balance was positive. A decision was made to explore the possibility of organizing an EPA summer school and creating an EPA Newsletter. The newly-elected SC was installed formed by N. Getoff (Austria), E. Vander Donckt and G. Delzenne (Belgium), O. Buchardt (Denmark), G. Quinkert and E.W. Schlag (Germany), J. Joussot-Dubien and J. Kossanyi (France), V. Balzani and U. Mazzucato (Italy), E. Havinga (The Netherlands), H.D. Becker (Sweden), H. Labhart and K. Schaffner (Switzerland), D. Bryce-Smith and G.D. Short (United Kingdom). The new SC met the day after and elected the following EC: K. Schaffner (Chairman) (Figs 3 and. 4), D. Bryce-Smith (Vice-Chairman), J. Kossanyi and U. Mazzucato (Secretaries) and O. Buchardt (Treasurer). To this list E. A. Koerner von Gustorf was added as a Special Secretary for gathering and disseminating information.

Fig. 3. Prof. Kurt Schaffner, the second President (1972-1976) (from EPA-NL n.58, p.48).

The new SC, according to article 9c of the Statutes, invited Israel (by considering the common western culture that Europe and Israel have in common), Poland and the USA to be represented on the Committee. E. Fischer, Z. Grabowski and O.L. Chapman, respectively, agreed to serve as representatives. Moreover, the new SC decided to produce an up-dated survey of European photochemical laboratories and to organize an EPA summer school in the near future. U. Mazzucato and J. Kossanyi, respectively, were entrusted to take care of planning these activities. The SC expressed a negative opinion regarding the creation of a new photochemical journal to avoid too much scattering of photochemical information.

Fig. 4. The two first (Derek Bryce-Smith, DBS) and second (Kurt Schaffner, KS) Presidents of the Association at the meeting on "Organic photochemistry and its synthetic applications" to celebrate the retirement of DBS (Readings, September 1991). Left to right: P. Wender, J. Pavlik, DBS, S. Davidson, KS, P. Sammes and A. Gilbert. (from EPA-NL n. 43, p. 39).

The plentiful correspondence between the Chairman and the members of the EC and the SC that followed the Reading meeting dealt with various aspects of the EPA activities, but mainly focused on economic aspects. While the responses of the governmental sources and national scientific organizations in the different countries to the requests for financial contributions were not real encouraging, there was a satisfactory rate of growth. Israel (The Academy of Sciences and Humanities) and Italy (C.N.R.) made substantial contributions, but thanks to the efforts of Prof. Labhart, the Swiss Federal Government gave the most, with an annual contribution of

S.F. 20,000. In the meantime, since many applications for travel grants to attend meetings and to visit different laboratories started to arrive, a scientific advisory board, chaired by D. Bryce-Smith, was nominated to evaluate such applications. The bank account of EPA was obviously open in Copenhagen, the town of the treasurer. J.A. Barltrop and D. Döpp were appointed as auditors.

Meetings of the EPA Committees, particularly of the EC, were held during the biennium to discuss the problems that arose during these first years of the young Association. Biennial meetings of the GC were planned on the occasion of international photochemical congresses of a general character, particularly the biennial IUPAC Symposium on Photochemistry. The program of activities established at the Reading meeting was successfully fulfilled in the biennium 1972-1974.

J. Kossanyi, with the assistance of O. Buchardt, organized the first EPA summer school, which was held in Reims (local organizer Prof. J.P. Pete) in September 1974 with successful participation and scientific level of lectures. In this decade, further EPA summer schools were organized in Leuven (September 1976) by F.C. De Schryver and in Rimini (September 1979) by V. Balzani.

The publication of the new directory of the photochemical laboratories, compiled by the author, met with serious difficulties at the beginning since the Committee for Higher Education and Research of the Council of Europe refused, mainly for economic reasons, to publish a revised up-dated version of the issue compiled by M. Fischer and published by the Council in 1970. Anyway, an up-dated edition was considered important by the Association because of the rapid developments in photochemistry and because the EPA had members in a number of countries not included in the previous report. At the end, the EPA accepted the offer of Elsevier-Sequoia S.A. to publish the new directory in September 1974 as Supplement No.1 of the Journal of Photochemistry. The new edition dealt with 230 laboratories and almost 900 researchers in 22 countries (18 from Europe). A Supplementary List to the Directory was published in the Oct. 1979 issue of the EPA-NL, pp.13-16.

During this period the Association sponsored several scientific meetings, such as the VII and VIII International Conferences on Photochemistry (in Jerusalem, August 1973, and Edmonton/Alberta, July 1975, respectively), the Conference on "Excited state of biological molecules" (Lisbon, April 1974), the Euchem Conference on "Useful synthetic aspects of photochemistry" (Ghent, September 1975) and the Microsymposium on Photochemistry and Photophysics of Coordination Compounds (Ferrara, July 1976). It also tried to develop closer relationships with the Eastern-European countries and, in June 1974, J. Kossanyi visited Poland and Hungary to make important contacts.

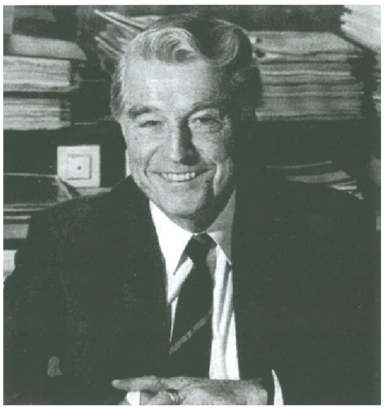

Fig. 5. Albert Weller, Vice-President from 1974-1976 (from EPA-NL n. 58, p. 7).

The 1974 meetings of the various bodies of the EPA were held on the occasion of the V IUPAC Symposium on Photochemistry in July 1974 in Enschede (Belgium). A joint meeting of the out-going and newly elected Standing Committees was held on July 22nd. Most of the old members were re-elected for a second term but there were also new names on the SC for the 1974-76 biennium (F.C. De Schryver for Belgium, H. Brodthagen for Denmark, P. Courtot for

France, E. Ratajczec for Poland, J.J. Bonnet for Spain and A. Gilbert for The United Kingdom). The SC elected the new EC: K. Schaffner, President, A. Weller, Vice-President (Fig. 5), O. Buchardt, confirmed as Treasurer, J. Kossanyi and U. Mazzucato, confirmed as Secretaries with the addition of J. Grabowski as third Secretary (Fig. 6). E. A. Koerner von Gustorf agreed to remain as Special Secretary. Two auditors (D. Döpp and H.D. Becker) were appointed.

Fig. 6. The three EC Secretaires from 1974-1976. From the left: Jean Kossanyi, Ugo Mazzucato and Zbigniew R. Grabowski (from EPA archives).

At the 1974 meeting it was announced that the membership had increased to about 360 members in 22 countries. The Treasurer presented a positive balance. It was decided to conform the membership fee to the equivalent of 30 D-Kr. The young members were encouraged to take advantage of the travel grants available for training and research purposes. In the biennium 1972-74 eleven requests were received and nine were granted. The Granting Advisory Board, chaired by D. Bryce-Smith, was confirmed. Finally, because of the untimely death of Th. Förster a few months earlier, the EC and SC proposed (and the GC approved) to inaugurate an annual EPA lectureship (the "Förster Memorial Lectureship") to commemorate his contributions to photochemistry and to the Association. A distinguished photochemist, chosen by a special commission in collaboration with local host institutes, is invited to tour and lecture in at least a couple of countries. The first Förster lecturers were George Porter in 1975, Z. Grabowski in 1976 and A. Weller in 1979.

A meeting of the EC was held in Reading in September 1975 to discuss various aspects of the ordinary management of the Association (summer school 1976, financing of the EPA, recruitment of new members, travel grant policy, promotion of national EPA Sections and preparation of the next SC and EC elections). The atmosphere of the EC meeting was very saddened by the fact that one of its members, Ernst Koerner von Gustorf, had died four days earlier.

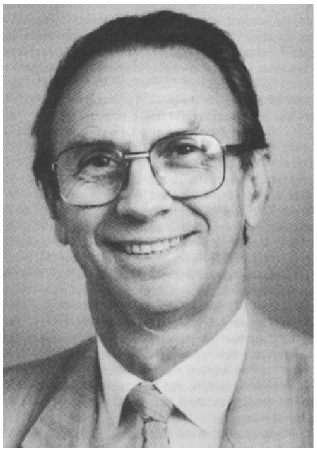

Fig. 7. Jacques Joussot-Dubien, the third President (1976-1980) of the EPA (from EPA-NL n. 62, p. 23).

At the end of the 1974-76 biennium, the various divisions of the EPA met again on the occasion of the VI International Symposium on Photochemistry in Aix-en-Provence (July 1976) where Jacques Joussot Dubien was elected Chairman (Fig. 7). The new Treasurer was U.P. Wild and the bank account of the Association was transferred to the Union Bank of Switzerland in Zurich.

The new President was very active in establishing scientific contacts with other countries and successfully organized the French-Japanese Colloquium on Photochemistry (Bordeaux, October 1979, in collaboration with P. Courtot) and the Trans-Pyrenees Informal Meeting on Photochemistry (Bombannes, France, May 1981). Moreover, under his chairmanship, an expanded and regular printed edition of the EPA-Newsletter started to appear in January 1978.

3. The EPA in its mature period (1977-2000)

After the detailed report on the founding of the EPA and its activities during the first decade, the principal events of the mature Association in the following decades are now summarized. At the end of the 1970s, the EPA had reached a membership of approximately 600 photochemists from some 24 countries. The membership dues for 1979 were SFr. 15. New members from new countries joined the Association, i.e., from Norway and The Soviet Union. It should be noted that from the beginning of the Association an annual Membership List was published. Statistics regarding the trend of individual memberships indicates the rapid increase from about 200 members from 20 countries in 1972 to a slightly fluctuating number of over 800 members from 32 countries in 1983 and over 900 from more than 40 countries in the following years. At the end of the 1970s, close contacts were established with the recently created Inter-American Photochemical Society (IAPS) and the Japanese Photochemistry Association (JPA).

In July 1978, the EPA Committees held a meeting in Leuven (VII IUPAC Symposium, Chairman N. J. Turro) and on that occasion Joussot-Dubien was confirmed as Chairman, F.C. De Schryver was appointed as Vice-Chairman and A. Gilbert and H.-D. Becker as Secretaries. The needs and possibilities of cooperation and joint action of the three Societies (EPA, IAPS and JPA) were examined, particularly the coordination of photochemistry meetings and the possible publication of a common journal. A. Lamola and a special committee of the IAPS, including representatives of the two sister Societies, established contacts with various publishers to discuss the issue.

The VIII IUPAC Symposium on Photochemistry was held in Seefeld (Austria) in July 1980. The proposal to establish a journal patronized by the three Photochemistry Associations was discussed further. A proposal was made to work out an agreement with Elsevier Sequoia, publisher of the Journal of Photochemistry, to try to expand the scope of the existing (physically oriented) journal with the creation of a Part B, more concerned with organic, inorganic and synthetic photochemistry, thus encompassing all aspects of the field. The new Committees of the EPA were installed. The EC was composed of F. De Schryver (Chairman, Fig. 8), F. Scandola (vice-Chairman), H.-D. Becker and F. Wilkinson (Secretaries) and J. Wirz (Treasurer). H. J. Kuhn was nominated Special Secretary for Memberships.

Fig. 8. Frans De Schryver, fourth President (1980-1984) of the EPA. (from EPA archives).

At the beginning of the second decade of life, the main problems faced by the Association were the publication of a new edition of the Directory of Photochemical Laboratories and the question of a common journal with the three Photochemistry Societies. B. Holmström from Göteborg accepted the task of preparing the updated Directory with the help of the EPA Secretary H.-D. Becker and the Editors of the Newsletter, G.R. De Maré and H.J. Kuhn. An expanded edition was published by Elsevier-Sequoia in 1981 as Supplement No. 2 of the Journal of Photochemistry. It dealt with some 400 laboratories and some 1500 researchers from 25 European and 9 non-European countries.

Instead, the publication of the new journal encountered several difficulties, i.e., the required guarantee of 500 subscriptions from the Societies as well as other problems that did not allow the initiative to be successful. At the end of 1980, the JPA decided not to proceed further for the moment and a little later the EPA also decided not to go ahead with the venture.

It is interesting to note that the increased contacts promoted by the Association led to the organization of several joint meetings of National EPA Sections such as those of the French-German Sections (Strasbourg, Nov. 1984), Italian-Swiss Sections (Como, 1987), Italian-French Sections (La Baume-les-Aix, Oct. 1989) as well as the 1st Mediterranean Meeting in Santa Tecla, Catania, in 1991, the Central European Photochemistry Conference (Krems, Austria, Oct.1993), the French-German meeting in Strasburg in 1994, the French-German-Swiss meeting (Konstanz, 1996), the German-Israeli Symposium on Photoinduced Processes (Mülheim, April 1997) and the German-Austrian-Italian meeting (Badgastein, Austria, March 1998), the latter being successfully followed by other editions.

During this period the EPA continued to run Summer Schools for young photochemists. The one in 1982 was in Königswinter (Germany), organized by H.-D. Scharf (Fig. 9), followed by those in Nordwijk, The Netherlands (J. Cornelisse and J. Lugtenburg, Sept. 1986) and in Spiez, Switzerland (A.M. Braun, 1989). The latter was the first one organized in cooperation with the Inter-American and Japanese Photochemical Societies and dedicated to interdisciplinary research (Fig. 10). Following Summer Schools were in Rimini, Italy (F. Barigelletti, 1992), in Noordwijk, The Netherlands (J. Verhoeven, 1998) and in Egmond aan Zee, The Netherlands (F. Brouwer and L. De Cola, summer 2003). The organization of the EPA Summer Schools is presently continuing at 2-3 year intervals.

Fig. 9. Participants in the 4th EPA Summer School, Königswinter, Germany, Sept. 1982 (from EPA-NL n. 16, p. 29).

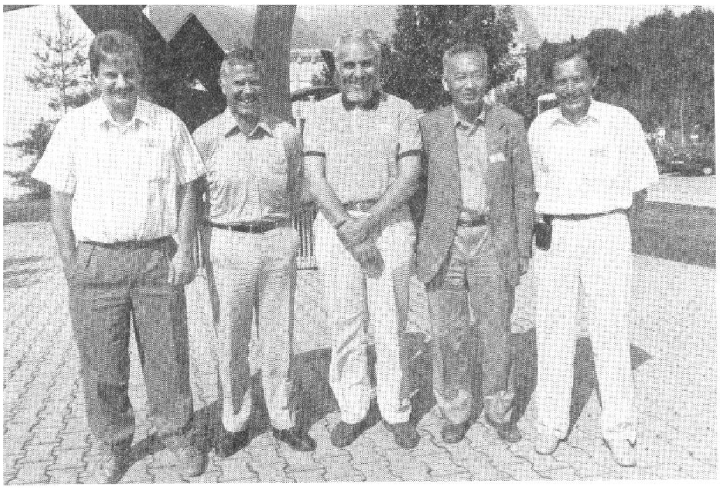

Fig. 10. The organizing staff of the 6th EPA Summer School 1989 on "Light and Pharmaceutical Chemistry" in Spiez, Switzerland, August 1989. From the left: T. Oppenländer, A.M. Breun, H. –J. Hansen, K. Tokumaru and B. Frei (from EPA-NL n. 37, p. 29).

The General Council meetings continued to be held on the occasion of the IUPAC Symposia on Photochemistry. The 1982 GC was held in Pau, France (IX Symposium). The EC was re-confirmed with only the replacement of H.-D. Becker with H. Dürr. In 1984 the GC was held in Interlaken (X IUPAC Symposium) where the question of a Society Journal was raised once more. The new EC was elected: F. Wilkinson (Chairman, Fig. 11), F. Scandola (Vice-Chairman), H. Dürr and H. Bouas-Laurent (Secretaries) and J. Wirz (Treasurer). The report of the 1983 EPA financial transactions was approved with a total credit of ca. SFr. 61,500 with an increasing trend (it will be over SFr. 80,000 in 1987). In this period the Association numbered more than 800 members.

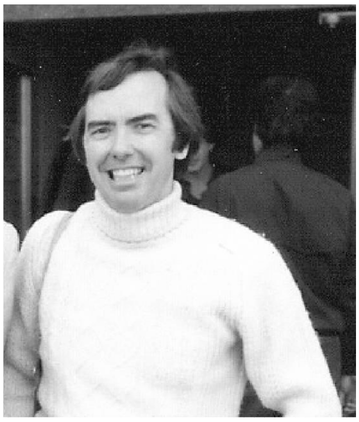

Fig. 11. Frank Wilkinson, 1984-1988 President of the EPA (from EPA archives)

The 1986 meeting of the GC was in Lisbon (XI IUPAC Symposium) (Fig.12). The members of the EC that had finished their second term were replaced by V. Balzani (Vice-Chairman), K.H. Grellmann (Secretary) and E. Haselbach (Treasurer). The GC devoted a large part of their discussion to the question of an International Journal of Photochemistry to be supported by the three societies, analysing the arguments in favour and against managing a Journal. It was re-confirmed that the Journal should be considered an expansion (Part II) of one of the existing journals published by Pergamon (Photochemistry and Photobiology) and Elsevier (Journal of Photochemistry). The GC voted to proceed further with negotiations.

Fig. 12. Musical event at the XI IUPAC Symposium on Photochemistry (Lisbon, July 1986). The picture shows the local hosts (Sebastiao Formosinho and Silvia Costa) and Frank Wilkinson (1984-1988 EPA Chairman) assisting a group of fado singers at the Conference banquet (from EPA-NL n. 28, p. 55).

The 1988 GC was held during the XII IUPAC Symposium on Photochemistry in Bologna. This was really a special occasion because the Symposium intended to celebrate the 900th anniversary (1088-1988) of the Bologna University (Fig. 13) and the genius figure of Giacomo Ciamician.

On that occasion, in a suggestive traditional ceremony, the University of Bologna bestowed the "Laurea ad Honorem" on Sir George Porter (Fig. 14). Moreover, the Ciamician medal, a prize offered by the Gruppo Italiano di Fotochimica (EPA section) to a scientist who had distinguished himself for his pioneering work in the field of photochemistry, was awarded to Albert Weller (Fig. 15) and the Sigillum Magnum, the silver symbol of the old University, offered to the most renowned visitors, was given to Jean-Marie Lehn.

Fig. 13. Left: Sigillum Magnum, the silver symbol of Bologna University (from EPA-NL n. 33, p.3) and right: Chairman V. Balzani opens the Congress (from archives of the Ciamician Institute of Bologna University).

Fig. 14. Ceremony of the "laurea ad honorem" bestowed on Sir George Porter at the XII IUPAC Symposium. From the left: two Faculty Members (V. Balzani and S. Focardi), the Rector of the

Bologna University (Prof. F. Roversi-Monaco) and Sir George (from archives of the Ciamician Institute of Bologna University).

Fig. 15. Albert Weller receives the Ciamician medal from Prof. V. Carassiti (University of Ferrara) (from EPA-NL n. 34, p. 54).

In addition, F. Wilkinson presented the "Porter Medal Fund" established by the ex-students and other research collaborators of Sir George. The first founding medal, which will be given biennially to scientists who have made the greatest recent contributions to photochemistry, was awarded to Sir George himself. The following medals were awarded to Michael Kasha, USA (1990)(Fig. 16), Kenichi Honda, Japan (1992) (Fig. 17), Nicholas Turro, USA (1994) (Fig. 18), J.C."Tito" Scaiano, Canada (1995), Noboru Mataga, Japan (1996), Frans de Schryver, Belgium (1998), Vincenzo Balzani, Italy (2000), Josef Michl, USA (2002), Graham R.Fleming, USA (2004), Howard E. Zimmerman, USA and Hiroshi Masuhara, Japan (2006) and David Phillips, UK (2010).

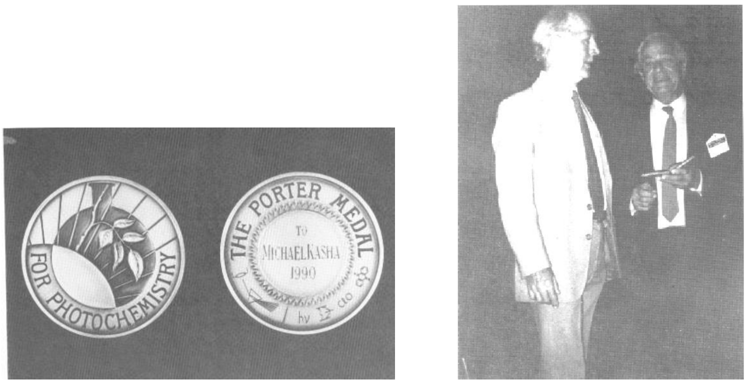

Fig. 16. Presentation of the Porter Medal to Michael Kasha by Lord Porter at the XIII International Symposium on Photochemistry, Warwick, UK, July 1990 (from EPA-NL n. 40. p. 27).

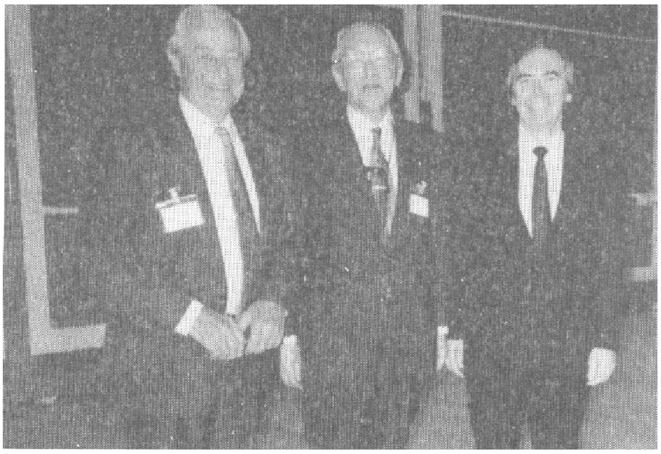

Fig. 17. Porter Medal award to Prof. Honda, Leuven July 1992. From the left: Lord Porter, Kenichi Honda and Frank Wilkinson (from EPA-NL n. 46, p. 21).

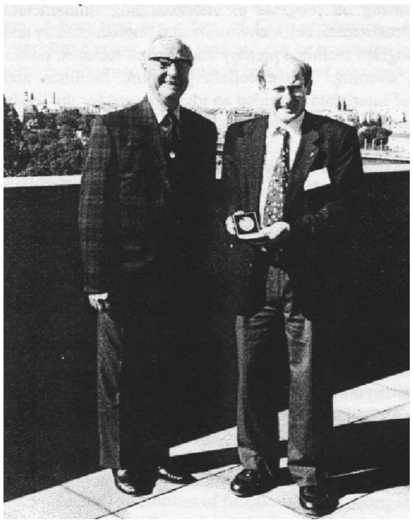

Fig. 18. Nick Turro, Porter Lecturer at the XV IUPAC Symposium (Praha, July 1994). From the left: Lord Porter, the medal and Nick Turro (from EPA-NL n. 52, p. 83).

Fig. 19. Prof. Egbert Havinga (from EPA-NL n. 6, p. 8).

In this connection, also the Havinga Medal has to be mentioned, given by the Stichting Havinga Fonds, established in Netherland in 1979 in honour of Prof. E. Havinga (Fig. 19) on the occasion of his retirement (awarded in 1990 to K. Schaffner and in 1991 to M. A. Fox).

The GC in Bologna elected the new EC: V. Balzani (Chairman, Fig. 20), R.S. Davidson (Vice-Chairman), K.H. Grellmann, E. Poquet and T. Vidoczy (Secretaries), while E. Haselbach was confirmed as Treasurer. An amendment to article 9a of the EPA Statutes was approved, establishing that "only countries with 30 members or more can have two members on the Standing Committee".

Fig. 20. Prof. Vincenzo Balzani, 1988-1992 President of the EPA and recipient of the Porter Medal 2000 (From EPA-NL n. 70, p.63).

The GC discussed important issues about the question of the common journal. After four years of negotiations, an agreement was approved among the three sister Societies (EPA, IAPS and JPA), the publisher (Pergamon Press) and the American Society of Photobiology to institute a two-year trial programme to expand Photochemistry and Photobiology in order to include photochemical papers of types that were not currently published in the journal. A successful trial period, dependent on the number of papers submitted and new subscriptions, would have led to a final decision about the division of the Journal into two parts, one corresponding to the current journal and the other containing photochemical papers largely unrelated to photobiology. This would lead the three Societies to run directly a separate section on Photochemistry and Photobiology with obvious scientific and financial advantages. The agreement was signed in November 1988.

Up to the end of the decade, there had been scarce participation of Eastern European countries in the Association. This started to improve also thanks to the presence of a Hungarian photochemist (T. Vidoczy) on the EC. In the summer 1989, a national group was constituted in the GDR and officially joined the EPA and a few months later the Academy of Science of the USSR decided to found a Soviet branch chaired by Prof. M.G. Kuzmin. The organization of national groups also started in other Eastern European countries. In that period a competition was launched among the EPA members to propose an appropriate logo for the EPA symbolizing its aims and activities.

Important international meetings were sponsored by the EPA in the 1980s, such as the first European Postgraduate Symposium on Photochemistry (London, April 1984, R.S. Davidson, Fig. 21), the International Meeting to honour the outstanding EPA member Lord George Porter, Nobel Laureate 1967 (London, July 1986, co-organizers D. Phillips and F. Wilkinson) and the Euchem Conference on Photoisomerism and rotamerism in organic molecules (Assisi, July 1988, U. Mazzucato).

The series of the Postgraduate Symposia continued in 1986 in Mülheim, Germany (H. Rau and M. Demuth), in 1988 in Jadwisin, Warsaw, Poland (St. Paszyc and J Herbich), in 1995 in Canterbury, Kent, UK (S. Davidson), and in 1997 in Mülheim again (M. Demuth).

In 1985 the Swiss EPA-Section founded the Grammaticakis-Neumann Prize (sponsored by Dr. Grammatikakis in honour of Dr. Neumann, a specialist in political sciences at the University of Vienna) for younger researchers of university and industrial institutions who had successfully contributed to the domain of photochemistry.

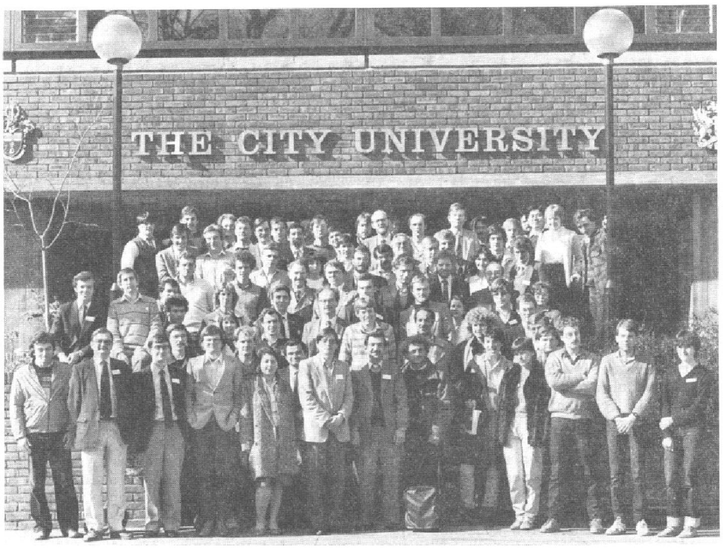

Fig. 21. Above: Participants of the European Postgraduate Symposium on Photochemistry, London, April 1984; below: the organizer staff, from the left: T. J. Kemp, J. D. Coyle, F. De Schryver, D. Goodwin and R. S. Davidson. (From EPA-NL n. 21, p. 18).

The first prize was awarded in 1985 to A. Harriman (GB) and I. Gould (USA). Following winners were M. Demuth (Germany, 1987), W. Rettig (Germany, 1990, Fig. 22), V. Ramamurthy (USA, 1991), M. van der Auweraer (Belgium, 1992), P.F. Aramendìa (Argentina, 1994), L. De Cola (Italy, 1995), M.B. Zimmt (USA, 1996), A.G. Griesbeck (Germany, 1997), W. Nau (Germany, 1999), E. Vauthey (Switzerland, 1999), D. Guldi (USA, 2000), N. Armaroli (Italy, 2001), J. Hofkens (Belgium, 2003), D. Bassani (France, 2005), T. Fiebig (USA) and A. Wagenknecht (Germany, 2006), A. Credi (Italy, 2007), A. Heckel (Germany, 2008) and S. Jayarman (USA, 2009). In other years (e.g. 2002 and 2004) no prize was awarded because no suitable candidate was proposed.

Fig. 22. Wolfgang Rettig receives the Grammaticakis-Neumann prize for 1990 from E. Haselbach (from EPA-NL n. 40, p. 24).

The 1990 meeting of the GC was held in July in Warwick (XIII IUPAC Symposium). V. Balzani (Chaiman) and Vidoczy (Secretary) were re-elected, while the new members of the EC were J. Verhoeven (Vice-Chairman), E. Migirdicyan (Secretary) and A. Braun (Treasurer). H.J. Kuhn was appointed as Managing Editor of the Newsletter and the Editorial Board was expanded with new members of both Western and Eastern Europe.

After three rounds of the competition for an EPA logo, a call for the EPA members to vote on the many sketches proposed from different countries was announced in March 1990. Since the not so many ballots received were in favour of different proposals, it was decided to forward the best suggestion to an artist in order to create the final version. U. Mazzucato asked for the help of designer Mr. F. Latini in Perugia. His proposal was presented at the GC of 1992 in Leuven and received such a full acclaim that it was decided that it should be the basis for the final printed version of the EPA logo (Fig. 23) which was put into action by A. Braun and H.-J. Kuhn (a detailed story of the logo by J.W. Verhoeven can be found in issue n.49 (November 1993) of the Newsletter.

After a period of standstill in assigning the Förster memorial lecture, in 1991 the EPA agreed that "Fachgruppe Photochemie der Gesellschaft Deutscher Chemiker" together with "Deutsche Bunsengesellschaft für Physikalische Chemie" should organize the granting procedure in the future. The 1991 Lecture was awarded to F.P. Schäfer (Göttingen), that of 1997 to D. Möbius (Göttingen) and to F. De Schryver (Leuven) in 1999/2000.

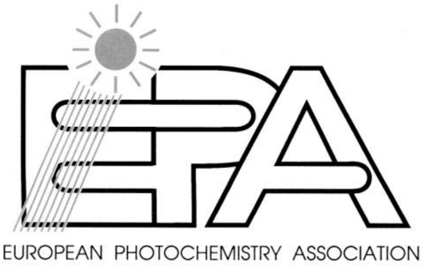

Fig. 23. The EPA logo.

The 1992 meeting of the GC was held in July in Leuven (XIV IUPAC Symposium). J. Verhoeven was appointed as new Chairman (Fig. 24), J. Wirz as Vice-Chairman, D. Döpp and M.G. Kuzmin as Secretaries. E. Migirdicyan was re-confirmed as Secretary and A. Braun as Treasurer. The financial situation was considered stable, with 75% of the income from membership fees (SFr. 25 per member) used to cover the increasing cost of the Newsletter. The most important problem in that period was to expand, as much as possible, collaboration between Western and Eastern laboratories. It was decided to sponsor some photochemical meetings, such as those organized in 1993, to honour Sidney Leach (Paris) and Nikola Getoff (Vienna). Even if the EPA in general did not financially support the organization of scientific events, the request of sponsorship/patronage to international and national meetings was encouraged. As bad news, it was announced that the agreement for the common journal "Photochemistry and Photobiology" between Pergamon and the three Societies had failed because the number of subscribers and submitted papers were too few.

Fig. 24. Jan Verhoeven, Chairman 1992-1996 [reproduced from PPS 9 (2010) 883].

The next meeting of the GC, SC and EC was held in July 1994 in Praha (XV IUPAC Symposium). The EC was unanimously re-elected with the only replacement being that of E. Migirdicyan (after her second term) by G. Favaro (Perugia) as Secretary. As for the financial situation, the membership fee was increased to SFr. 30 (SFr. 20 for students and retired members). As in the previous biennium, a sum of SFr. 4000 was set aside to offer travel grants for young photochemists. It was announced that the EPA would continue to be an organization associated with IUPAC. After the XIX Membership List of the EPA, issued in November 1994, it was decided to make the list available on the EPA website and up-date it biennially. T. Vidoczy's proposal to set up an EPA electronic database in his Institution in Budapest (Photochemistry on the Internet) to help exchange of information was approved by the GC.

Fig. 25. Participants of the 4th Solar Conference, Cairo, Jan. 1997 (from EPA-NL n. 59, p.98).

In this period the Association started to sponsor two biennial series of important meetings, such as the International Conference on Solar Energy and Applied Photochemistry (SOLAR), held biennially in Egypt (Fig. 25) and the International Symposium on Photochromism (ISOP, Fig. 26).

The next GC meeting was in Finland (XVI IUPAC Symposium, Helsinki, July 1996). The new EC was elected: J. Wirz (Chairman, Fig. 27), J.-P. Pete (Vice-chairman), S. Canonica (Treasurer), G. Favaro, A. Vlcek, jr., I. Soboleva (Secretaires). The balance, which had remained constant at about SFr.70,000, was unanimously approved. In line with the earlier initiative of T. Vidoczy in Budapest, a new EPA homepage was developed at the Chairman's laboratory in Basel.

Fig. 26. Participants of the ISOP 96, the 2nd International Symposium on Photochromism, Clearwater Beach, Florida, Sept. 1996 (from EPA-NL n. 58, p. 120).

Fig. 27. Jacob Wirz, Chairman of the EPA, 1996-2000 (from EPA-NL n.75, p.17).

In 1997, G. Grabner in Vienna compiled and continually up-dated a comprehensive database of the literature dealing with photochemistry and related fields. A link to that site could be found on the EPA homepage. At the 1998 GC in Sitges, Barcelona, the EC in charge was re-confirmed.

In 1999 H.J. Kuhn, after a splendid period of service as Managing Editor of the NL for many years, asked to be replaced and J. Kossanyi was appointed to this task.

The next GC meeting was held in Dresden in 2000 (XVIII IUPAC Symposium). The Chairman proposed some changes to the EPA Statutes. In particular it was established that one of the rights and functions of the GC is "to elect biennially the members of the new EC from the candidates proposed by the SC and the EC". The new EC was elected: J. Waluk (Poland) as Chairman (Fig. 28), W. Rettig (Germany) as Vice-chairman, H. Lemmetyinen (Finland) and S. Monti (Italy) as Secretaires. S. Canonica was re-confirmed as Treasurer with H. Görner and W. Horspool as auditors.

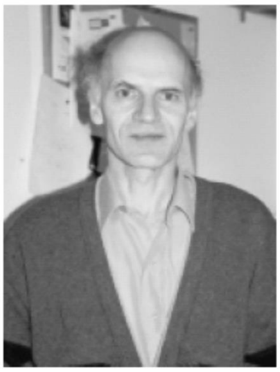

Fig. 28. Jacek Waluk, the 2000-2004 Chairman of the EPA, 2000-2004 (from EPA archives).

On that occasion, the new Chairman again took up the discussion on the subject of a new journal and planned to nominate a task force for further contacts with publishers and the sister Societies. It has to be noted in this respect that in that period, the European Society for Photobiology (ESP) had planned to start a journal that would have replaced the Journal of Photochemistry and Photobiology, Part B and that the ESP contacted the EPA with the offer to join their initiative, becoming co-owners and co-editors.

The new Chairman asked the EPA members to express their opinion on this proposal. It is also interesting to recall that the Chairman, considering the close links of the photochemists with relative areas (physics, spectroscopy, biology, etc.), also made some comments about the current idea that the term "Photoscience" could be more attractive and useful than "Photochemistry". At Dresden, two refreshing historical treatises on photochemistry in the 20th century and on the IUPAC Symposia on Photochemistry were presented by Heinz Roth and Kurt Schaffner, respectively.

Fig. 29. Werner Nau (Univ. Basel, center) and Eric Vauthey (Univ. Fribourg, right) receive the Grammatikakis-Neumann prize 1999 from Jacques Moser (chairman of the awarding Committee, left) (from EPA-NL n. 68, p. 25).

A successful Graduate Student Symposium was organized on February 2000 in Fribourg by T. Bally. In that occasion the 1999 Grammatikakis-Neumann prize was given to Werner Nau (Univ. Basel) and Eric Vauthey (Univ. Fribourg) (Fig. 29).

4. EPA in the last decade: a slackening period and a prompt revival

At the beginning of 2001, a new organization, the Inter-Society Committee on the Practice of Photosciences, was established to replace, in some way, the former IUPAC Photochemistry Commission. Direct links with the sister Societies were assured and S. Braslavsky (Fig. 30) was nominated as the EPA representative whose function was to become important for developing related fields of research.

Fig. 30. Silvia Braslavsky, representative of EPA on the IUPAC Photochemistry Commission. (from EPA-NL n.69, p. 27)

In the same year, the task forces of the EPA and ESP succeeded in reaching an agreement for a new journal (Photochemical and Photobiological Sciences, PPS), jointly owned by the two Societies and published by the Royal Society of Chemistry. J.F. Bornman (Denmark) and F. Wilkinson (UK) were nominated Editors-in-Chief, and J. Wirz (Switzerland) and J. Piette (Belgium) as Deputy Editors-in-Chief. The Presidents of the two sister societies (IAPS and JPA) agreed to serve on the Editorial Board of the new journal.

In this period the series of joint meetings among different national EPA sections, very stimulating to promote profitable collaboration, continued to be organized, such as those of the Belgium-Italy-Netherlands sections (Noordwijk, The Netherlands, 1999), of the Italian, French and Swiss Photochemistry Groups (Lausanne, 2001, Fig. 31) and the 2nd Mediterranean Meetings on Photochemistry (Giardini Naxos, Sicily, 2003).

The next GC meeting of the EPA was held in Budapest (XIX IUPAC Symposium) in July 2002. The EC was unanimously re-elected. The meeting supported the proposal to make the electronic version of PPS available for each EPA member and made important decisions about the future of the Newsletter (see Appendix).

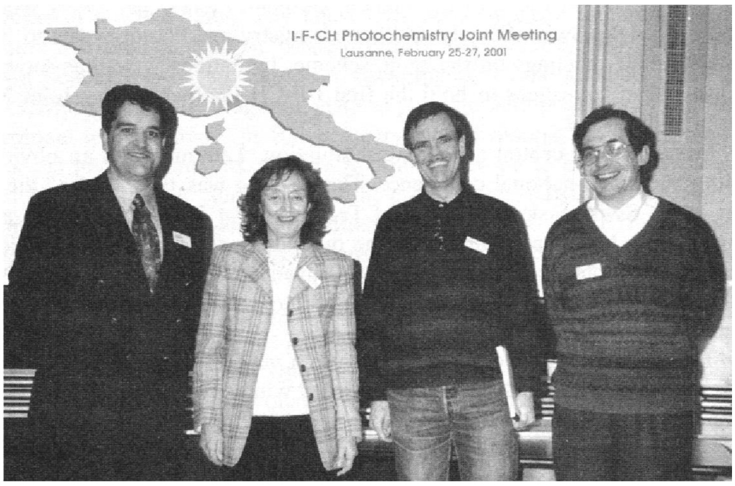

Fig. 31. Joint meeting of the of the French-Italian-Swiss meeting of the EPA sections (Lausanne, 2001). Left to right: the Chairman Jacques Moser and the three Presidents, Giovanna Favaro,Thomas Bally and Robert Pansu (from EPA-NL n. 72, p. 8).

The 2004 GC meeting was held in Granada (XX IUPAC Symposium). W. Rettig was nominated for the new Chairmanship, but he was unable to take up the position due to poor health. The GC appointed the new EC: D. Phillips (Chairman, Fig. 32), E. Vauthey (Switzerland), D. Markovitsi (France) and N. Gritsan (Russia) as new Secretaries. H. Lemmetyinen (Finland) and S. Monti (Italy) were re-confirmed as Secretaries and S. Canonica as Treasurer. The membership fee was increased to 30 Euro (15 for students) mainly because of the increasing cost paid by the EPA for free access of its members to PPS.

Fig. 32. David Phillips, Chairman of the EPA, 2004-2007 (from EPA archives).

At the end of 2004 the EPA members received the sad news of the untimely death of Jean Kossanyi, a friend photochemist who had been very active in many EPA activities and more recently as Managing Editor of the Newsletter. During this period several members started to complain about the absence of hard copies of the NL and to ask why there was a notable slowing down in its production in general (printed and online). The Chairman D. Phillips recognized that the renewed management of the Association and particularly the long illness and final loss of the Editor were the main reasons for this situation.

Later on the Chairman (see his Editorial in the on-line EPA-Newsletter of May 2006), while recognizing that the Association had been suffering in the last period and that membership and activity had declined, expressed interesting comments on the situation. He considered that the cohesion of researchers in photochemistry, which was the main goal of the Association at its very beginning, was now dissipating into other organizations concerned with specific or transversal subjects. Decline in the membership in several countries was a consequence of such movement as well as of the ageing of the original pioneering supporters, who had worked with so much enthusiasm. Decrease in the membership and increase in the cost of PPS meant that almost the entire EPA membership fee was used for the contribution to PPS. As a consequence, the Chairman urged that a big effort be made by the national representatives of EPA to increase EPA membership in all countries to help revive the Association. In the same Editorial, the Chairman announced his intention, on the occasion of his retirement from the Imperial College, to give up the Chairmanship of the EPA.

A meeting of the EC was held in London in March 2006. H. Lemmetyinen was appointed Vice-Chairman, while E. Vauthey and D. Markovitsi took on the roles of Website Manager and Newsletter Editor, respectively. Instead of at the up-coming XXI IUPAC Symposium (Kyoto, 2006), it was decided that a new Chairman and a new EC should be elected on the occasion of the GC meeting to be convened in Cologne in July 2007 on the occasion of the XXIII International Conference on Photochemistry. The EC also decided to offer a prize for the best PhD Thesis in Photochemistry. The initiative had a huge success, which continued in the following years. It was also decided to revise the Statutes of EPA to adapt them to the changes in the scientific and institutional context of the European community.

Fig. 33. Dimitra Markovitsi, President of the EPA, 2007-2010 (from EPA archives).

At the next GC meeting in Cologne, Dimitra Markovitsi succeeded David Phillips as Chairman of the EPA (Fig. 33). The other members of the EC were re-elected. The past Chairman remained as a member of the EC, who was complemented by D. Worrall (UK), who became the new Editor of the NL, and Werner Nau (Germany). At the meeting, Sarah Ruthven, associate member of the Editorial Board of the PPS (in the meantime R. Tyrrell, UK, and F. De Schryver, Belgium, had been appointed as Editors-in-Chief), made a positive survey on the current quality of the journal (part-owned by EPA and published by RSC). It was happily noticed that PPS had reached the highest impact factor of all photochemical/biological journals (it reached 2.71 in 2009). On the other hand, it was also once again emphasized that the subscription cost exceeded the EPA membership fee thus causing a decline in the EPA finances.

The GC met in Gothenburg in 2008 (XXII IUPAC Symposium) and approved the revisions to the EPA Statutes presented by the EC. They decided to re-elect the current EC, assigning specific tasks to each member: Dimitra Markovitsi (France, Chairman), Helge Lemmetyinen (Finland, Vice-Chairman), Silvio Canonica (Switzerland, Treasurer), Nina Gritsan (Russia, Membership), Werner Nau (Germany, Public Relations), David Phillips (UK, Past Chair), Sandra Monti, Italy, PPS matters), D. Worrall (UK, Editor of NL) and E. Vauthey (Switzerland, Website Manager). At the meeting, the two first winners of the PhD Prize for the best thesis in the field of photochemistry (Maria Abrahamsson, Sweden, and Alexander Fürstenberg, Switzerland) presented their work.

As written in the Chairman's Editorial of December 2008, the Association had recently started a drive towards making photochemistry known to the wider public. The Chairman and the Past-Chairman had represented the EPA at the Conference "Opening up scientific research to learning communities" held in Athens in September 2008. The fact that 2011 would be the International Year of Chemistry would offer the opportunity to give a real image of chemistry to the wider public and to publicize how photochemistry plays a role in many related fields, such as biology and cultural heritage, environmental chemistry, nanotechnologies and so on.

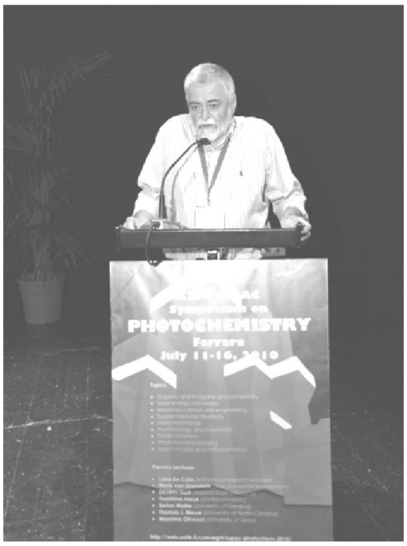

Fig. 34. Franco Scandola (chairman) opens the XXIII IUPAC Symposium (Ferrara, July 2010) (from EPA archives)

The last 2010 GC meeting was in Ferrara (XXIII IUPAC Symposium)(Fig. 34). It was an occasion to hear the talks of Anne Kotiaho, the winner of the second Prize for the PhD thesis, W. Nau, winner of the EPA-PPS award, and D. Phillips, recipient of the 2010 Porter Medal.

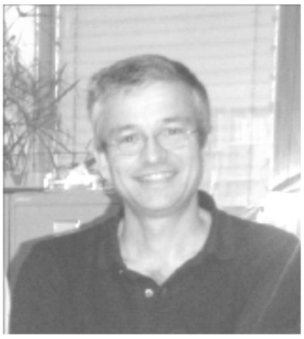

Fig. 35. Eric Vauthey, President of EPA in force (2010-)
(from EPA archives).

The new EC was also elected. Eric Vauthey (Fig. 35) was elected the new Chairman, Dimitra Markovitsi remained on the Committee as Past-President and S. Canonica as Treasurer. The other members were John Gilchrist (UK, Industry-Liaison), Olga Fedorova (Russia, Public Relations), Werner Nau (Germany, Responsible for PPS matters), Bo Albinsson (Sweden, Newsletter Editor), Julia Pérez-Prieto (Spain, Associate Editor) and David Worrall (UK, Website manager).

In the satellite meeting "Ciamician Paternò Heritage Photosciences, a look into the future", organized by A. Albini, Dimitra Markovitsi explained how it could be a good opportunity for the EPA to be involved in an activity aimed at popularising photochemistry in the framework of the 2008-2010 e-knownet project "Information and Communication Technologies enabled non-formal science learning", supported by the European Lifelong Learning Programme.

At the end of this review, it is dutiful to sadly mention that two of the co-founders and active Chairmen of the EPA left us in the last years:

Jacques Joussot-Dubien, the third President, on May 2009, aged 81, and Derek Bryce-Smith, the first President, on June 2011, aged 85.

The number of the 2011 memberships (the list on the EPA web-site reports less than 500 members but it is certainly not yet complete) seems to be still quite a bit less compared with the period 1980-2000. Such huge decrease probably depends much on the activity of the national sections and representatives, otherwise it would be difficult to explain why countries with similar numbers of active photochemical laboratories and similar production in the field have quite different numbers of associated researchers. Obviously, as said above, the decline in enthusiasm plays an important role too. Anyway, at the end of the first decade of the new century, after some sort of lethargy, the Association has shown signs of revival, thanks to the big efforts made by the Chairmen and the various Committees during this last period. It is also important that the Association has definitively resolved the problem of the Journal, which has been a thorny problem of EPA for decades. After ten years of life, the Photochemistry Photobiology Sciences is now an international journal of high reputation, meeting the growing information needs of scientists working in the areas of photochemistry and photobiology, and indeed, encourages a synergism between these two important research areas. At present the journal, which maintains a quite satisfactory impact factor, is published monthly on behalf of the European Photochemistry Association (EPA), the European Society for Photobiology (ESP), the Asia and Oceania Society for Photobiology (AOSP) and the Korean Society of Photoscience (KSP), and is available in both printed and electronic formats. The affiliation of the two eastern societies with *Photochemical & Photobiological Sciences* as their new official journal fosters the promotion and development of photochemistry and photobiology at an intercontinental level. Also the continuation of the schools, meetings and prizes organized and/or sponsored by the Association and other initiatives under study offer good occasions to revive the spirit of the Association and to realize that it is at work The next 2012 GC meeting (XXIV Symposium) to be held in Coimbra, Portugal will offer a nice occasion to feel the pulse of the EPA and to make new projections.

Appendix - The history of the EPA Newsletter

During the first years of the EPA life, distribution of information among the members was entrusted to typewritten circular letters. In January 1978, under the chairmanship of J. Joussot-Dubien, when the Association was approaching maturity, an expanded printed edition of the EPA Newsletter (at a professional-like printing and binding level) started to be regularly published on a quarterly basis (sometime less). S.G. Boué from the Free University of Bruxelles and H.J. Kuhn from the Max-Planck Institut für Strahlenchemie in Mülheim a.d. Ruhr were appointed Editors of the Newsletter. It should also be recalled that the Institute in Mülheim had been so helpful (with Koerner von Gustorf at the beginning and later with H.J. Kuhn) in solving the Association's printing problems.

As outlined by the Chairman in the first issue, the aim of the Newsletter was to include essentially permanent columns on the following items: editorials from the Chairman and the bodies of the EPA; announcements of forthcoming events in the field of photochemistry (conferences, summer schools, workshops, etc); general news from the international scientific scenery; personal news (deaths, anniversaries, nominations, etc.); theses, new books, book reviews, and job openings . Other desirable reports on EPA activities (relations with other scientific organizations, scientific highlights of meetings with photographs, presentation of photochemical laboratories and new equipment, financial reports, short reports on present and future trends in special fields of photochemistry, commercial messages, letters from members and humour) were also considered and, in fact, have been published now and then.

In 1979 G.R. De Maré replaced S.G. Boué as co-Editor of the Newsletter with H.J. Kuhn. In 1982 H. Dürr joined them as the third co-Editor. The Newsletter became more and more attractive with the publication of the series History of Photochemistry (pioneers and trends), Photochemistry in Europe, Technical Reports, Topical Articles, the news about Glossary of Terms used in Photochemistry (from the IUPAC Commission) and regular news from the sister Societies (IAPS and JPA). Nevertheless, in the July 1986 issue, the Editors of the Newsletter published a complaint against the scarce contributions received from the EPA members asking for more active participation from the "silent members", estimated to be 95%.

It was interesting to read the editorials in the EPA-NL by V. Balzani in the 1988-1992 period of his chairmanship. Besides the routine discussion of the EPA activities, his comments devoted considerable attention to real questions, mainly political and social problems, such as the risks and real disasters of the war in the Middle East, the central role of chemistry in a civilized society, the new horizons for photochemistry, *.i.e.,* the movement from molecules to supermolecules, how to fight against the bad reputation of chemistry which causes lack of students and funding, and similar topics. Also very interesting were the editorial reflections of the next Chairman, J. Verhoeven, but devoted to different (scientific/philosophical) topics such as the interactions between light and matter, usefulness of computerization to (photo)chemists, creativity and innovations in research, etc. At the end of 1980s, the EPA-NL called for advertisements giving the advantage to firms producing instruments of interest for photochemical work to make their products better known to a highly competent readership.

Fig. 36. Dr. Hans Jochen Kuhn, who edited for many years the Newsletter (from EPA-NL n. 67, p.1).

The EPA Committees met in July 1990 in Warwick and appointed H.J. Kuhn as Managing Editor (Fig. 36) and expanded the Editorial Board adding to the former co-Editors, G.R. De Maré and H. Dürr, other five new members: H. Hennig (Leipzig, Germany), J. Herbich (Warsaw, Poland), J. Kossanyi (Thiais, France), U. Mazzucato (Perugia, Italy) and M.G. Kuzmin (Moscow, USSR).

In the early 1990s the Newsletter had reached its maturity and its articles were selectively abstracted in Chemical Abstracts. The NL, really the main activity of the Association, was of crucial importance as a vehicle of communication among photochemists. It was considered a real point of strength of the EPA, mainly thanks to the efforts of the Managing Editor, who dedicated time and energy to this job. The NL continued to be prepared and printed at the Max-Planck Institut of Mülheim under his ever inspiring and tireless activity. The collaboration established with IAPS and JPA had further enhanced its international character. Regular publication of photochemical topics received from the IUPAC Commission on Photochemistry, as was done in the past with the "Glossary of Terms used in Photochemistry", was considered of great use to the readers.

On the occasion of the 20th anniversary of the Newsletter, the author's reflections about its good health and its improvements, based on a comparison of the contents between the first and second decades, appeared in n. 61, November 1997. In the same issue, since there was no index for about the 60 EPA-NLs published in this period, the Editor started to publish a series of overviews of articles, reviews and notes of various nature that had been published in the first two decades to help readers to find articles that could be of lasting interest.

Starting in 1994, EPA was accessible on the Internet. This created perplexities about the role of the printed version of the NL, which was the core service of the Association, but its printing and distribution had also used up most of its resources. Therefore, considering also that the funding from governmental agencies and national foundations had virtually dried up in that period, the proposal for the future publication of the NL on the Internet and e-mail distribution started to be requested by various members.

In 1999 the bad news of Jochen Kuhn's wish to be replaced as the Managing Editor of the NL (yet remaining on the Board) started to circulate. In n. 67 of the NL (November 1999), the Chairman gave the official news in his editorial where he recognized the splendid service of Jochen since the beginning and his merit for the high standard reached by the NL and its usefulness as the medium for communication among photochemists. J. Kossanyi was appointed as Managing Editor, while G. De Maré and M. Kuzmin were replaced on the Editorial Board by M. Demuth (Germany), A. Parusel (Austria), J.-P. Pete (France) and F. Wilkinson (UK).

The GC meeting in Budapest 2002 made important decisions about the future of the Newsletter, namely to shift the scientific articles of the EPA-NL to PPS, leaving the NL mainly devoted to the EPA news, to publish only one printed issue per year and to publish bimonthly (or more) electronic issues on the EPA website. This decision became effective soon and the regular production of the printed NL ceased with issue n. 76 at the end of 2002. The next printed issue (n. 77) appeared only in February 2004 and the next one in June 2008. The EPA-NL passed through a series of difficult circumstances in that period because of the parallel suffering situation of the Association (see above), but specifically due to the Editor's long illness, which culminated in his sad and premature death in December 2004 (see a tender obituary by K. Schaffner in the on-line NL issue of May 2005). A willing volunteer, Mohamed Sarakha (France), took over as provisional Editor and did his best in that not-easy situation. At the meeting of the EC in London in March 2006, Dimitra Markovitsi was appointed Editor of the NL but after her nomination as Chairman in 2007, the position passed to David Worrall (UK).

In the meantime several EPA members lamented about the absence of a printed version and a small pocket-booklet seemed to be more attractive than navigating on the website. The EC tried to meet these requests half way, so in 2006 the NL started to appear more regularly with two issues per year, generally one electronic and one printed. In the meantime the printing had moved from Mülheim to Tournos, France, then, after brief periods to Warszawa and Bologna; it is now printed in Loughborough, UK, managed by D. Worrall. At the 2010 GC meeting in Ferrara, Bologna, Bo Albinsson (Sweden) was appointed new Editor of the EPA Newsletter and Julia Pérez-Prieto (Spain) Associate Editor.

Acknowledgements. The author is grateful to Eric Vauthey, EPA Chairman, for his interest in the matter, to Hans Jochen Kuhn, past Editor of the EPA Newsletter, and all other colleagues who gave a precious help in collecting the pictures of this review article.

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Pulsed Laser Ablation: role of photochemical processes

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1. Introduction

Pulsed Laser Ablation (PLA) is the expression used to describe the explosive evaporation which occurs when a high energy pulsed laser beam power is focussed onto a solid. Although this phenomenon has been named as Laser Evaporation, Laser Sputtering, Laser Etching etc., nowadays it is generally known as Laser Ablation. On the contrary of the previously mentioned definitions which describe only a small part of the whole physical process involved, the Laser Ablation name has been chosen in order to consider all phenomena implicated and therefore avoid any possible misunderstanding.

The interaction of a laser beam with a solid target produces the ejection of atoms, ions, electrons, molecules, clusters and, in many cases, particulate. All these components give origin to the laser ablation characteristic plasma which expands preferentially along the normal to the target, even though the other two spatial dimensions are anyway involved. The plasma speed normal to the target, that is of the order of 10^2-10^5 ms^{-1}, is related to the travelling particles type, the ablation laser wavelength, pulse duration and energy, and, of course, to the deposition environment background pressure. The basic equipment required for PLA experiments consists of a vacuum chamber containing a rotating target, a substrate holder and several windows for the laser inlet and the plasma analysis. A typical apparatus is schematised in Figure 1. In general the laser hits the target at an angle of 45° and any kind of pulsed laser can be suitable for PLA, although a sufficiently high power laser beam requirement, whose value depends on the target material in use, must be satisfied. Laser beams in the UV-vis region are usually preferred to IR ones because of both their higher photon energies and limited thermal effects on the target surface. Nonetheless, IR and, in particular, near-IR lasers are also used for many applications.[1]

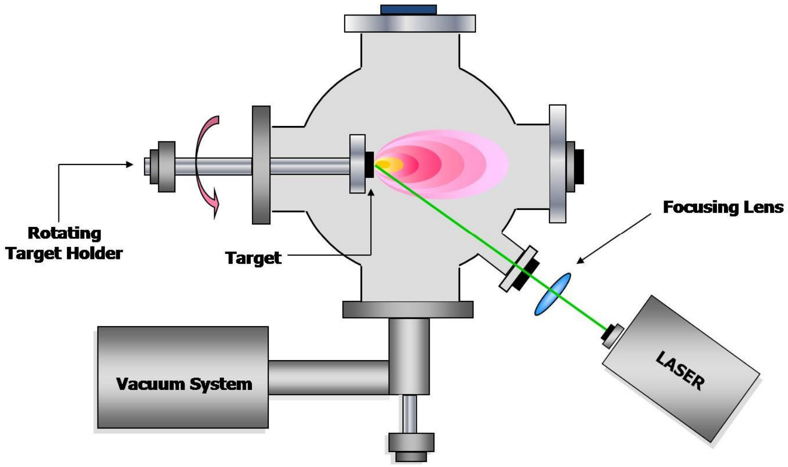

Figure 1. Experimental set-up for PLA experiments in vacuum.

When a focused pulsed laser beam irradiates a solid target, two different interaction regimes, photothermal and photochemical, can be involved. Photothermal laser ablation concerns the fundamental mechanism of interaction between laser and solid, and the time scale for the thermalization of the excitation energy. If the laser ablation is thermally activated, it can be described by the temperature and total energy changes. Photochemical laser ablation is determined by the degree of selective excitation. In other words, thermal ablation refers to a mechanism in which phonons, generated as a result of non-radiative transitions or of electron-lattice interactions, lead to a partial emission of material by vibrational motion. In the case of photochemical laser ablation, or, more precisely, electronic induced laser ablation, an accumulation of electronic excitation leads directly to electron-hole pairs formation and bond breaking. From this point of view, in many cases the first steps of laser-matter interaction are photochemical phenomena. In literature there are many detailed and comprehensive works on both laser-matter interaction[2-5] and PLA applications[6] and in this paper the attention will be focalized only on the photochemical processes. In particular we will consider only the processes involving the solid surface and not those related to the molecular or atomic species adsorbed on this surface even if laser photochemistry of molecules bonded to a solid surface or adsorbed on it is often related to the electrons ejected from the surface, by single or multi-photon absorption phenomena.

2. Photochemical processes on the solid surface.

The interaction of the laser radiation can induce different photochemical phenomena on the solid surface, depending on the characteristics of the solid.

In case of metals the radiation can induce the emission of electrons, if the photon energy is higher than the metal photoemission threshold, or their excitation. The energy of the excited electrons is converted into kinetic energy and then dissipated through electron-electron collisions, allowing thermalization. At this point the electrons transfer energy to the lattice. Depending on laser pulse duration, the consequence can be the heating and melting of the surface of the material (short pulses) or the direct vaporization of the first layers of the target material (ultra-short pulses).[7] In both cases the processes can be considered of photothermal type, so only the emission of photoelectrons can be useful for our discussion, as we will see later.

In case of semiconductor or insulators the effect of the radiation can be the production of electron-hole pairs or the formation of defects. The mechanisms of electron-hole pairs formation can be various (Figure 2). Obviously, if the photon energy is higher than the material energy gap the pairs can be produced by single photon excitation but also multi-photon absorption and defect-enhanced absorption processes are possible ways for electron excitation. In these two last cases, the photon energy can be lower than the energy gap. In particular multi-photon absorption can be achieved by the sequential absorption of several photons.

This mechanism, however, presents smaller absorption cross sections than single photon transitions, and therefore the probability of a transition is low. For example, in single-photon band-to-band transition $\sigma \approx 10^{-17}$ cm^2, whereas for multi-photon band-to-band transition $\sigma^{(2)} \approx 10^{-34} - 10^{-50}$ cm^4 s^{-1}, $\sigma^{(3)} \approx 10^{-51} - 10^{-80}$ cm^6 s^{-2}, $\sigma^{(4)} \approx$

10^{-68} - 10^{-140} cm^8 s^{-3}, where *(2)*, *(3)* and *(4)* is the order of the multi-photon transition.[2] On the other hand, transitions associated with defects have $\sigma \approx 10^{-16}$ - 10^{-20} cm^2, and their excited state energies dwell within the material band gap. Consequently, electron transitions can easily involve defect excited states by single-photon absorption. These defect excited states can relax by direct ejection of weakly bonded atoms (WBAs) from the specimen surface, or can induce a metastable state by configuration changes in the system surrounding the lattice. The configuration changes are due to local lattice deformations, causing alterations of the WBAs inter-nuclear bond distances. In this way, a further weakening of WBAs bonds is induced, and their ablation is generated through consecutive laser photon absorption.[8]

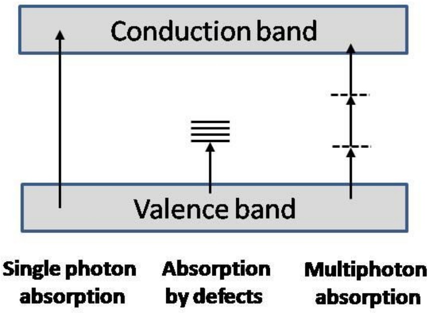

Figure 2. Scheme for different types of laser electronic excitation in solids.

For a perfect crystal, the laser ablation process can be explained by the creation of defects. In this regard, two different routes should be considered: (1) solids with weak electron-lattice coupling (semiconductors) and (2) solids with strong electron-lattice coupling (insulators). For the former, absorption of the incident radiation produce free electron-hole pairs by multi or single-photon transitions for $E_g > h\nu_L$ and $E_g < h\nu_L$ respectively. These free charge carriers can be trapped in lattice sites with the electrons in an anti-bonding orbital and the hole in a bonding orbital of a lattice bond, causing lattice deformation (localised state for electron-hole pairs). If this lattice deformation overcomes the Coulombian repulsion energy, another hole can be trapped on the same bonding orbital and a second electron can go into the previously singly occupied anti-bonding orbital. The consequence of this phenomenon is the breaking up of the lattice bond, with formation of a defect. On the other hand, for case (2), laser beam absorption produces excitons. The excitons are electron-hole pairs in bonded energy states with levels lower than the conduction band edge. The exciton movements, as opposed to the case of free electron-hole pairs, create a strong local deformation in the lattice as a result of induced movements of their coupled charge carriers (e.g. polarons). Such lattice deformations give rise to new localised states, called self trapped excitons (STEs), where the excitons are confined. STEs, as well as free electro-hole pair localised states, can relax through either a radiative or a non-radiative path. There are two different kinds of non-radiative relaxation: defect formation and defect excitation. Defect formation (mechanisms (1) and (2) as discussed above) can traslate, for example, into colour centres and/or Frenkel pairs and/or other types of defects.[9] Alternatively, from the free electron-hole pair localised state or the STE state, relaxation can involve the release of energy onto a pre-existent defect site. In this way, no new defect is created but an existing defect is excited. The pre-existing defects involved in non-radiative relaxation arise from previously described mechanisms (1) and (2) or from intrinsic defects already present in the solid.

In addition, since the lower edge of the conduction band is close to the vacuum level, the electrons promoted, by multi or single photon absorption, at a distance from the target surface lower than their free path, can leave the surface itself and photoelectrons emission can be detected.

A large number of experiments showing direct evidence of ablation by a non-thermal mechanism are reported in literature. Of particular interest are the results obtained for ablation carried out by ultra-short laser sources. In fact, ultra-short PLA (laser pulse time duration of 1 ps or less) offers numerous advantages compared to PLA performed by longer pulse lasers, especially for applications in the deposition of thin films of materials with technological interest.[10]

For example, in the irradiation of different dielectric samples by an ultra-fast pulse (100 fs) Ti:sapphire laser with a photon energy of 1.55 eV, the mission of photoelectrons has been detected.[9] Since the laser photon frequency is in the NIR, the electrons excitation across the band gap requires multi-photon absorption. In the case of BaF_2 and CaF_2 the absorption could also involve the presence of localized or transient defect states.[11,12] In the same systems, in conditions of low laser intensity, the emission of positive ions and large clusters has been evidenced by Time of Flight mass spectrometry.[13] All the detected species show the same kinetic energy which means that they are not formed by reactions among the ablated materials but are directly ejected from the target. A possible ejection mechanism is related to the already cited emission of electrons under the laser irradiation. This phenomenon occurs in a very short time, during the laser pulse, and the electrons leave positive hole in the region near the surface. Since the time of neutralization of the holes by bulk electrons is quite long (picoseconds or more), the surface will remain positively charged for some time. This process causes an electrostatic surface instability and, for a density of hole sufficiently high, the resulting perturbation of the target lattice results in the emission of positive particles, from atomic ions to larger clusters of more than ten atoms. These charged particles are accelerated by the residual electrical field and the overall material emission in this conditions is known as "Coulomb explosion".[14-16] When the electronic excitation is higher, corresponding to a higher laser intensity, a fast coupling between the electrons and the lattice, through electron-phonon collisions, takes place, leading to the formation of an overheated surface layer and if the heating is rapid enough, leading the system near its thermodynamic critical temperature where explosive phenomena, like phase explosion,[17] can take place. In this case the release of material, now in the form atoms, molecules, clusters and nanoparticles, can be very high and can be treated as a photothermal process.

3. Conclusions

In conclusion both photothermal and photochemical processes are involved in the description of Pulsed Laser Ablation phenomena. The photochemical processes play an important role especially in the laser- matter interaction involving dielectric materials but, in general, are the basic absorption processes for all types of solids. For laser intensities below and near the ablation threshold, these processes are surely the most important but their role cannot be neglected also when there is a massive ejection of material. From this point of view, the understanding of photochemical processes is also important when PLA is used for technological applications such as thin films deposition.

References.

1. Saenger, K.L. in *Pulsed Laser Deposition of Thin Films*, D.B. Chrisey and G.K. Hubler (Eds.), John Wiley & Sons, New York, 1994, p. 582.
2. Haglund, R.F.; Itoh, N. in *Laser Ablation*, J.C. Miller (Ed.), Springer - Verlag, Berlin, 1994, p. 11.
3. Mele, A.; Giardini Guidoni, A.; Flamini, C.; Latini, A.; Orlando S.; Teghil, R. *Proc. Indian Acad. Sciences (Chem. Sci.)*, **110**, 163 (1998).
4. Haglund, R.F. in *Laser desorption and Ablation*, J.C. Miller and R.F. Haglund (Eds.), Academic Press, San Diego, 1998, p.15.
5. Bäuerle, D. *Laser Processing and Chemistry*, Springer, Berlin, 2011.
6. Eason, R. (Ed.), *Pulsed Laser Deposition of Thin Films, Applications-Led Growth of Functional Materials*, John Wiley & Sons, Hoboken, 2006.
7. Anisimov, S.I.; Kapeliovich, B.L.; Perel'man, T.L. *Zh. Eksp. Teor. Fiz.*, **66**, 776 (1974).
8. Itoh, N.; Tanimura, K. *J. Phys. Chem. Solids*, **51**, 717 (1990).
9. Reif, J.; Costache, F. in *Advances in Atomic, Molecular and Optical Physics*, 53, M.O. Scully, G. Rempe (Eds.), Academic Press, 2006, p. 228.
10. Teghil, R.; D'Alessio, L.; De Bonis, A.; Ferro, D.; Galasso , A.; Lanza, G.; Santagata, A.; Villani, P.; Sordelet, D.J. *Thin Solid Films*, **517**, 1880 (2009).
11. Matthias, E.; Nielsen, H.B.; Reif, J.; Rosen, A.; Westin, E. *J. Vac. Sci. Technol. B*, **5**, 1415 (1987).
12. Rosen, A.; Westin, E.; Matthias, E.; Nielsen H.B.; Reif, J. *Phys. Scripta* **T23**, 184 (1988).
13. Reif, J.; Costache, F.; Eckert, S.; Henyk, M. *Appl. Phys. A*, **79**, 1229 (2004).
14. Reif, J. in *Laser-Surface Interactions for New Materials Production*, A. Miotello and P.M. Ossi (Eds.), Springer, Heidelberg, 2010, p. 19.
15. Stoian, R.; Ashkenasi, D.; Rosenfeld, A.; Campbell, E.E.B. *Phys. Rev. B* **62**, 13167 (2000).
16. Stoian, R.; Rosenfeld, A.; Ashkenasi, D.; Hertel, I.V.; Bulgakova, N.M.; Campbell, E.E.B. *Phys. Rev. Lett.* **88**, 097603 (2002).
17. Kelly, R.; Miotello, A. *Appl. Surf. Sci.*, **96**, 205 (1995).

Photochemistry Down Under – Solar Chemicals from and for the Tropics

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Introduction – Organic photochemistry started 'outdoors' on the roofs of chemical institutes as a solar discipline in the 19th century.[1] The potential of solar photochemistry was described over 100 years ago by a pioneer in organic photochemistry, Giacomo Ciamician.[2] In his visionary lecture *"The Photochemistry of the Future"* he imagined the replacement of hazardous, at that time coal-based, processes with clean, solar-driven alternatives.[3] A century has passed and his vision remains largely unfulfilled. Recently, the call for sustainable and climate-smart technologies has led to a revival of the sun as an energy and light source.[4] Modern solar concentrators were furthermore developed to accelerate reactions and increase space-time-yields.[5] Likewise, cost estimation studies have demonstrated that solar production can indeed operate economically.[6]

The *Applied and Green Photochemistry Group* at James Cook University (JCU) in Townsville, Australia, has been at the forefront of solar photochemical research and has realized solar transformations from laboratory through to production scales.[7] Located in tropical North Queensland, Townsville experiences over 300 days of sunshine per year, which makes it a favorable location for solar research. The current *Solar Chemicals from and for the Tropics* initiative of the group builds on both of tropical Australia's abundant natural resources, sunlight and biomass, and utilizes these for the bulk production of commercially and tropically relevant chemicals. Since sunlight excludes most of the highly energetic UV light, solarchemical transformations often proceed more cleanly and produce less side products. Compared to lamp-driven processes, this commonly reduces purification steps and results in better product qualities.

Solar reactors – The group at JCU operates a number of solar reactors for small to pilot-scale synthesis in sunlight (**Figure 1**). Small-scale illuminations are still commonly performed following the traditional 'flask in the sun' approach. Larger reactions are conducted in custom-made 1 m^2 flatbed reactors (<8 L capacity) and a 2 m^2 Compound Parabolic Collector (CPC; <50 L capacity). Both reactor types use direct and diffuse light and are operated in circulation mode. The unique "round-W" mirror shape of the CPC reactor additionally allows optimal capture of sunlight.

As part of a recent commercialization grant, the *Applied and Green Photochemistry Group* has synthesized pilot kilogram-batches of valuable commodity chemicals, within 1-3 days of solar exposure using flatbed or compound parabolic concentrator (CPC) reactors. The advantage of operating several different size solar reactors, as seen below, is that it allows for rapid feedback in process development, modifications and refinements. Because of this our preliminary results have received significant attention from local media and industry.

Based in costal North Queensland, the group at JCU is also investigating applications of 'solar floats' (developed by Prof. Liu at the University of Hawaii, USA).[8] These devices use natural water-reservoirs as heat-sinks and thus avoid the high cooling water demand of conventional lamp-driven processes or heat exchangers attached to solar reactors.

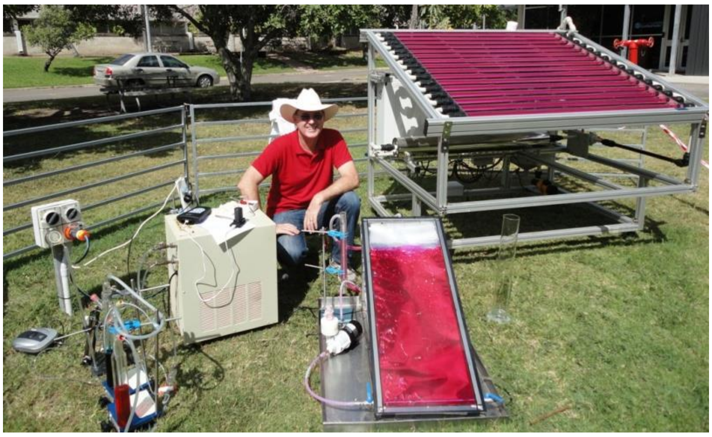
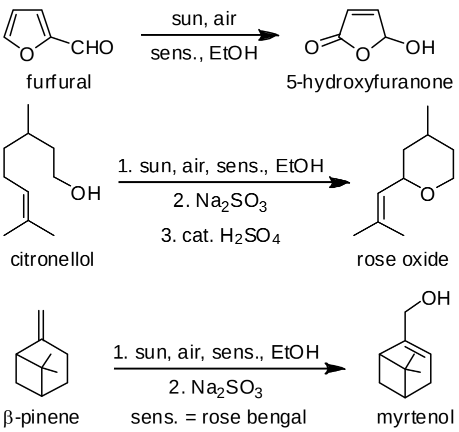


Figure 1. Matthew Bolte in between the solar reactors at James Cook University in Townsville, Australia.

Solar photoreactions – At JCU, the solar research activities are focused on photooxygenations of renewable materials (**Scheme 1**).[9] Air is commonly used as a safe and inexpensive oxygen source. Likewise ethanol, a renewable resource from the sugar industry, is employed as a non-hazardous solvent. The targeted commodity chemicals are of particular economic value for tropical North Queensland.



Scheme 1. Selected photooxygenations investigated.

Sugarcane bagasse from the local sugar industry, for example, represents an important fuel source and potential renewable feedstock. The transformation of furfural, a bagasse-derived compound, into high value chemicals is thus of strategic importance.[10] The photooxygenation of furfural into the versatile building block hydroxyfuranone proceeds in one step, without the need of further reduction.[11] In contrast, elevated temperatures furnish directly the corresponding alkoxy-derivatives as novel fragrances.[12] Similarly, Australia was a major producer of essential oils, however, increasing pressure from Asia and customer demands have seen a declining share of the world market. This has created a need for value adding and diversification of product portfolios. The conversion of essential oils into high end, natural fragrances thus addresses this need and opens innovative new markets.[13] The transformation of citronellol to the important fragrance rose oxide, for example, follows a simple three-step procedure.[14] The crucial photooxygenation step has been previously realized on large-scale using concentrated sunlight. The conversion of β-pinene to the low volume fragrance myrtenol via a two-step protocol is likewise investigated at JCU.[15]

Conclusion – Tropical Australia offers excellent opportunities for solarchemical research. Solar photooxygenations in particular allow for the easy conversion of renewable materials from the local agriculture and forestry industry into high-value chemicals of industrial importance.

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References.

1. H. D. Roth "The beginnings of organic photochemistry" *Angew. Chem. Int. Ed. Engl.* 1989, 28: 1193-1207.
2. G. Nebbia, G. B. Kauffman "Prophet of solar energy: a retrospective view of Giacomo Luigi Ciamician (1857-1922), the founder of Green Chemistry, on the 150th anniversary of his birth" *Chem. Educator* 2007, 12: 362-369.
3. G. Ciamician "The photochemistry of the future" *Science* 1912, 36: 385-394.
4. P. Esser, B. Pohlmann, H.-D. Scharf "The photochemical synthesis of fine chemicals with sunlight" *Angew. Chem. Int. Ed. Engl.* 1994, 33: 2009-2023.
5. (a) A. Fernandez-Garcia, E. Zarza, L. Valenzuela, M. Perez "Parabolic-trough solar collectors and their applications" *Renew. Sust. Energy Rev.* 2010, 14: 1695-1721; (b) K.-H. Funken, J. Ortner, "Technologies for the solar photochemical and photocatalytic manufacture of specialities and commodities: a review" *Z. Phys. Chem.* 1999, 213: 99-105.
6. (a) N. Monnerie, J. Ortner "Economic evaluation of the industrial photosynthesis of rose oxide via lamp or solar operated photooxidation of citronellol" *J. Sol. Energy Eng.* 2001, 123: 171-174; (b) K.-H. Funken, F.-J. Müller, J. Ortner, K.-J. Riffelmann, C. Sattler "Solar

collectors versus lamps – a comparison of the energy demand of industrial photochemical processes as exemplified by the production of ε-caprolactam" *Energy* 1999, 24: 681-687.

7. (a) M. Oelgemöller, C. Jung, J. Mattay "Green photochemistry: Production of fine chemicals with sunlight" *Pure Appl. Chem.* 2007, 79: 1939–1947; (b) M. Oelgemöller, C. Jung, J. Ortner, J. Mattay, E. Zimmermann "Green Photochemistry: solar photooxygenations with medium concentrated sunlight" *Green Chem.* 2005, 7: 35-38.

8. Y.-P. Zhao, R. O. Campbell, R. S. H. Liu "Solar reactions for preparing hindered 7-cis-isomers of dienes and trienes in the vitamin A series" *Green Chem.* 2008, 10: 1038-1042

9. (a) K. Gollnick "Photooxygenation and its application in chemistry" *Chim. Ind.* 1982, 63: 156-166; (b) W. Rojahn, H.-U. Warnecke "Die photosensibilisierte Sauerstoffübertragung – eine Methode zur Herstellung hochwertiger Riechstoffe" *DRAGOCO-Report* 1980, 27: 159-164; (c) M. Fischer "Industrial applications of photochemical synthesis" *Angew. Chem. Int. Ed. Engl.* 1978, 17: 16-26.

10. A. Mamman, J. Lee, Y. Kim, T. Hwang, N. Park, Y. Hwang, J. Chang, J. Hwang "Furfural: Hemicellulose/xylosederived biochemical" *Biofuels Bioprod. Bioref.* 2008, 2: 438-454.

11. (a) S. Marinković, C. Brulé, N. Hoffmann, E. Prost, J.-M. Nuzillard, V. Bulach "Origin of chiral induction in radical reactions with the diastereoisomers (5R)- and (5S)-5-l-menthyloxyfuran-2[5H]-one" *J. Org. Chem.* 2004, 69: 1646-1651; (b) G. O. Schenck "Über die unsensibilisierte und photosensibilisierte Autoxydation von Furanen" *Liebigs Ann. Chem.* 1953, 584: 156-176.

12. P. Esser, R. Pelzer, F. Völkl "Verwendung substituierter Lactone als Riechstoffe" *EP-0761808A2*, 1996 [*Chem. Abstr.* 1997, 138: 220667].

13. J. L. Bicas, A. P. Dionisio, G. M. Pastore "Bio-oxidation of terpines: an approach for the flavour industry" *Chem. Rev.* 2009, 109: 4518-4531.

14. G. Ohloff, E. Klein, G. O. Schenck "Darstellung von Rosenoxyden und anderen Hydropyran-Derivaten über Photohydroperoxyde" *Angew. Chem.* 1961, 73: 578.

15. G. O. Schenck, H. Eggert, W. Denk "Über die Bildung von Hydroperoxyden bei photosensibilisierten Reaktionen von O_2 mit geeigneten Akzeptoren, insbesondere mit α- und β-Pinen" *Liebigs Ann. Chem.* 1953, 584: 177-198.

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Publications

"Recommended Standards for Reporting Photochemical Data" Lamola, A.A.; Wrighton, M.S. *Pure Appl. Chem.* **1984**, *56*, 939-944.

"Reference Materials for Fluorescence Measurements" Eaton, D. *Pure Appl. Chem.* **1988**, *60*, 1107-1114.

"Recommended Methods for Fluorescence Decay Analysis" Eaton, D. *Pure Appl. Chem.* **1990**, *62*, 1631-1648.

"Molar Absorption Coefficients of Transient Species in Solution". Bonneau, R.; Carmichael, I.; Hug, G.L. *Pure Appl. Chem.* **1991**, *63*, 290-299.

"Methods for Production of Radical Ions in Low Temperature Matrices for Electronic Spectroscopy". Iwamura, H.; Eaton, D. *Pure Appl. Chem.* **1991**, *63*, 1003-1014.

"A Collection of Experiments for Teaching Photochemistry". Tokumaru, K.; Coyle, J.D. *Pure Appl. Chem.* **1992**, *64*, 1343-1382.

"Glossary of Terms Used in Photochemistry" 3rd Version (IUPAC Recommendations). Braslavsky, S.E. *Pure Appl. Chem.* **2007**, *79*, 293-456.

"Terminology, relative photonic efficiencies and quantum yields in heterogeneous photocatalysis. Part I: Suggested protocol". Serpone, N.; Salinaro, A. *Pure Appl. Chem.* **1999**, *71*, 303-320.

(cont)

"Terminology, relative photonic efficiencies and quantum yields in heterogeneous photocatalysis. Part II: Experimental determination of quantum yields" Salinaro, A.; Emeline, A.V.; Zhao, J.; Hidaka, H.; Ryabchuk, V.K.; Serpone, N. *Pure Appl. Chem.* **1999**, *71*, 321-335.

"Figures-of-Merit for the Technical Development and Application of Advanced Oxidation Technologies for Both Electric- and Solar-Driven Systems". Bolton, J.R.; Bircher, K.G.; Tumas, W.; Tolman, C.A. *Pure Appl. Chem.* **2001**, *73*, 627-637.

"Organic Photochromism" . Bouas-Laurent, H.; Dürr, H. *Pure Appl. Chem.* **2001**, *73*, 639-665.

"Chemical Actinometry", 2nd version (IUPAC Technical Report). Kuhn, H. J.; Braslavsky, S. E.; Schmidt, R. *Pure Appl. Chem.* **2004**, *76*, 2105-2146.

"Glossary of Terms used in Photocatalysis and Radiation Catalysis". Braslavsky, S. E.; Braun, E. M.; Cassano, A. E.; Emeline, A. V.; Litter, M. I.; Palmisano, L.; Parmon, V. N.; Serpone, N. *Pure Appl. Chem.* **2011**, *83*, 931-1014. Errata: *Pure Appl. Chem.* **2011**, *83*, 1215.

"Fluorescence standards: Classification, terminology, and recommendations on their selection, use, and production" (IUPAC Technical Report) Resch-Genger, U.; DeRose, P. C. *Pure Appl. Chem.* **2010**, *82*, 2315-2335.

"Standards for photoluminescence quantum yield measurements in solution" (IUPAC Technical Report). Brouwer, A. M. *Pure Appl. Chem.* **2011**, *83*, 2213-2228.

"Characterization of photoluminescence measuring systems" (IUPAC Technical Report). Resch-Genger, U.; DeRose. P. C. *Pure Appl. Chem.* Published on line, 2012-06-04

Various additional publications within the project **2004-021-1-300** on photoluminescence are either under revision or in press (Chairs: E. San Román and F. Brouwer)

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SPECIAL REPORTS ON ARTIFICIAL PHOTOSYNTHESIS

Dear EPA members,

This issue of the EPA Newsletter (June 2013) is dedicated to "Artificial Photosynthesis", currently a vital research area aimed at finding alternative sources and technologies for satisfying the demand for sustainable energy. We appreciate the effort of the experts in this field who have sent us significant reports summarizing their recent contributions to the design of systems inspired in Nature.

Gary F. Moore (Lawrence Berkeley National Laboratory) reports on a strategy for interfacing visible-light absorbing semiconductors with bio-inspired catalysts for hydrogen production. *Thomas J. Meyer et al.* (Energy Frontier Research Center, University of North Carolina) report on key molecular assemblies for dye-sensitized photoelectrosynthesis cells and solar fuels. *James R. Durrant et al* (Imperial College London) report on the advantages for producing of H_2 evolution by combining molecular catalysts and semiconductors and on the usefulness of transient absorption spectroscopy for studying the electron transfer processes in these hybrid systems. *Manuel J. Llansola-Portoles* reports on the evolution of the work of *Devens Gust, Thomas A. Moore, and Ana L. Moore group* (Center for Bioenergy and Photosynthesis, Arizona State University) focusing on the design of systems for artificial photosynthesis, ranging from the time when they began using organic chromophores as the reaction centers, to the present when they have designed a hybrid triad comprising a molecular dyad and a semiconductor nanoparticle.

In addition, *Stephanie Pendlebury* (Imperial College, London) introduces *the Solar Fuels Network* led by Prof. James Durrant and reports on the overall objectives of this Network, and their intention to carry out creative activities that aim to inform people of a wide range of ages and levels of scientific knowledge about on-going research and technologies related to photo(electro)chemical synthesis of fuels using sunlight.

The EPA Newsletter Board greatly appreciates these experts' contributions to this issue.

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Kinetic control in TiO_2 films functionalised with molecular dyes and catalysts for H^+ reduction

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The development of H_2 evolution photocatalysts is currently being expanded in different directions, ranging from homogeneous to heterogeneous systems.[1, 2] Recently, a new research area resulting from the combination of molecular catalysts and semiconductors in one photocatalytic system is gaining increasingly attention.[3] Hybrid systems can integrate the already developed molecular catalysts for H^+ reduction into a complete heterogeneous photocatalytic system.[4-6] Different types of systems have been studied, either by combining an electrocatalyst and a narrow band gap semiconductor as a sensitizer, or by co-functionalizing a wide band gap semiconductor with a molecular dye and a catalyst. These hybrid systems combine the high selectivity towards H^+ reduction offered by the molecular catalysts, with an enhanced charge separation due to electron transfer between the different components. In addition, the double reduction of a single molecular catalyst required for the solar driven fuel synthesis, leading to the formation of reaction intermediates, is more favourable than the accumulation of multiple electrons within one nanoparticle of a bare semiconductor.

The development of efficient hybrid photocatalytic systems involves the exhaustive study of the electron transfer kinetics between the different components and the control of the main recombination pathways. Transient absorption spectroscopy is a technique that can be used to monitor the lifetime of charge carriers in semiconductors (electrons and holes),[7, 8] as well as transient molecular species that absorb in the visible or near-infrared region.[9] In a recent work, we have used transient absorption spectroscopy to study the kinetics of electron transfer in a photocatalytic system for H_2 evolution at neutral pH, based on the functionalization of TiO_2 nanoparticles with a molecular ruthenium dye (RuP) and a cobaloxime catalyst (CoP) in the presence of a sacrificial electron donor (D) (Fig. 1).[10] A quantitative charge separation takes place through the ultrafast (180 ps) dye electron injection into the conduction band of the TiO$_2$ upon visible light excitation. Efficient dye regeneration by the sacrificial electron donor is necessary in order to generate long-lived electrons in the semiconductor, capable to doubly reduce the molecular catalyst. Although triethanolamine is a commonly used hole scavenger in dye sensitised photocatalytic systems,[11] we have observed that the slow regeneration of the oxidised dye by this sacrificial electron donor (~0.1 ms) results in the enhanced recombination of the photoinjected electrons with the oxidised dye (~0.1 ms).

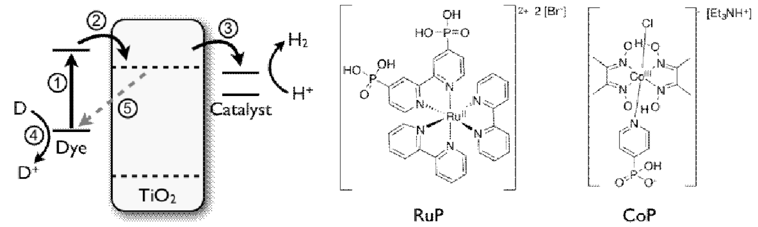

Figure 1. Schematic of electron transfer in a hybrid system composed of a semiconductor functionalised with a molecular ruthenium dye and a cobalt catalyst. The numbering refer to the following processes: 1) Dye + h3 → Dye*, 2) Dye* + TiO$_2$ → Dye$^+$ + e$^-$/TiO$_2$, 3) e$^-$/TiO$_2$ + Catalyst → TiO$_2$ + Catalyst$^-$, 4) Dye$^+$ + Donor → Dye + Donor$^+$, 5) Dye$^+$ + e$^-$/TiO$_2$ → Dye + TiO$_2$.

The catalytic mechanism of cobaloximes involves the sequential reduction of the molecular catalyst from Co^{III} to Co^{I}.[12, 13] The different kinetics of the two electron transfers from the TiO$_2$ conduction band to the molecular catalyst are related to the thermodynamic driving force of each reduction reaction. Considering the difference of 0.4 V in the redox potential between the first and second reduction of the cobalt catalyst ($E_{red(CoIII/II)}$ = -0.15 V vs NHE, $E_{red(CoII/I)}$ = -0.55 V vs NHE)[10], singly reduced cobalt species must be accumulated at the surface of TiO$_2$ before the second reduction reaction takes place (Fig. 2). Thus, the Co^{II}/Co^{I} electron transfer can be expected to be kinetically much slower than Co^{III}/Co^{II}, requiring the generation of long-lived TiO$_2$ electrons to enable efficient electron transfer to the catalyst. Experiments are on-going to address this limitation, and its impact upon the efficiency of solar driven hydrogen generation.

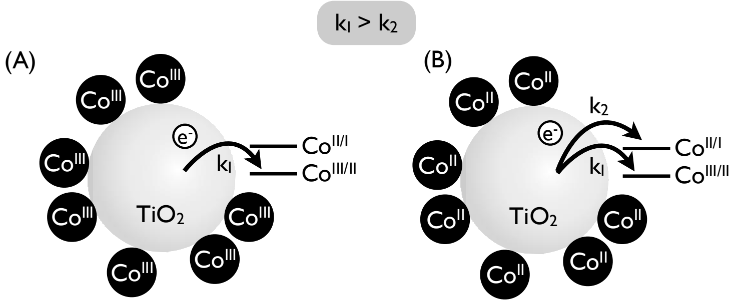

Figure 2. Diagram of the two-electron transfers in a TiO_2/catalyst system. (A) Thermodynamically, the Co^{III}/Co^{II} reduction reaction is more favourable, while the second reduction of the Co^{II}/Co^{I} catalyst requires the accumulation of a monolayer of singly reduced catalyst (B).

The control of the two-electron transfer kinetics, as well as the design of molecular catalysts with a low overpotential for the water reduction reaction are critical issues for the effective implementation of hybrid systems composed of a molecular catalyst and a semiconductor that require multiple reduction reactions. Understanding and addressing this challenge is likely to be critical in the development of solar to fuel conversion hybrid systems.

The work summarised herein has been done in collaboration with Dr. Erwin Reisner, Fezile Lakadamyali, Dr. Masaru Kato and Manuela A. Gross. Financial support from the ERC (project Intersolar) and the European Commission Marie Curie CIG (PCIG10-GA-2011-303650) are gratefully acknowledged.

References

1. Chen, X., Shen, S., Guo, L. , Mao, S. S. *Chem. Rev.* **110**, 6503-6570 (2010).
2. Eckenhoff, W. T. , Eisenberg, R. *Dalton Trans.* **41**, 13004-13021 (2012).

3. Tran, P. D., Wong, L. H., Barber, J. , Loo, J. S. C. *Energy Env. Sci.* **5**, 5902-5918 (2012).
4. Wang, M., Chen, L. , Sun, L. *Energy Env. Sci.* **5**, 6763-6778 (2012).
5. Losse, S., Vos, J. G. , Rau, S. *Coord. Chem. Rev.* **254**, 2492-2504 (2010).
6. Capon, J.-F., Gloaguen, F., Schollhammer, P. , Talarmin, J. *Coord. Chem. Rev.* **249**, 1664-1676 (2005).
7. Tang, J., Durrant, J. R. , Klug, D. R. *J. Am. Chem. Soc.* **130**, 13885-13891 (2008).
8. Yoshihara, T., Katoh, R., Furube, A., Tamaki, Y., Murai, M., Hara, K., Murata, S., Arakawa, H. , Tachiya, M. *J. Phys. Chem. B* **108**, 3817-3823 (2004).
9. Reynal, A. , Palomares, E. *Eur. J. Inorg. Chem.* **2011**, 4509-4526 (2011).
10. Lakadamyali, F., Reynal, A., Kato, M., Durrant, J. R. , Reisner, E. *Chem. Eur. J.* **18**, 15464-15475 (2012).
11. Song, W., Brennaman, M. K., Concepcion, J. J., Jurss, J. W., Hoertz, P. G., Luo, H., Chen, C., Hanson, K. , Meyer, T. J. *J. Phys. Chem. C* **115**, 7081-7091 (2011).
12. Dempsey, J. L., Winkler, J. R. , Gray, H. B. *J. Am. Chem. Soc.* **132**, 1060-1065 (2009).
13. Muresan, N. M., Willkomm, J., Mersch, D., Vaynzof, Y. , Reisner, E. *Angew. Chem. Int. Ed.* **51**, 12749-12753 (2012).

Molecular and Nanoscale Interfaces for a Global Scale Challenge

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A sustainable energy future demands alternative energy sources and technologies that cut the tie between energy use and net carbon emission.[1,2] Solar energy offers a promising approach to meeting these requirements, provided efficient, scalable, and durable systems can be developed for its collection, conversion, and storage. In the biological world, the sun's energy is harvested by photosynthetic organisms and is ultimately stored in chemical bonds via a complex series of enzymatic reactions.[3] Artificial photosynthesis (AP) is a long-sought goal in solar energy research. By splitting water into oxygen and a source of reducing equivalents (protons and electrons) for producing a fuel, two problems are addressed: energy storage and the production of a potential transport fuel. However, the goal of AP is not to chemically mimic every aspect of the biological counterpart. The challenge is to use these systems as inspiration for developing new technologies with a human agenda. For example, the efficiency of initial light capture and charge separation steps in natural photosynthesis is near unity; but losses due to inherited metabolic processes (legacy biochemistry) and use of intermediate energy carriers reduce the overall energy conversion efficiency to less than a few percent.[4,5] In principle, human engineered systems could bypass such constraints by having fewer energy transduction steps with improved interfaces.

AP will likely require strategies to engineer surfaces with molecular and nanoscale interfaces to materials that enhance the electronic quality, stability and catalytic functionality of the underlying substrate. A recent report in the *Journal of Physical Chemistry Letters* describes an approach to interfacing visible-light absorbing semiconductors, including *p*-type (100) GaP and *p*-type (111) Si, with bioinspired catalysts for hydrogen production.[6] The grafting procedure exploits the UV-induced immobilization chemistry of alkenes to a semiconductor surface,

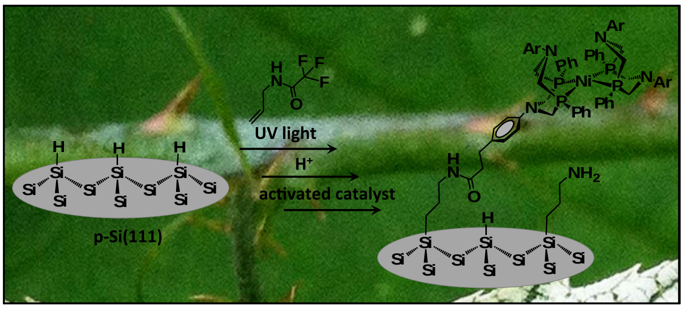

Figure 1. Synthetic scheme for interfacing *p*-type (111) Si with a bioinspired catalyst for hydrogen production (photo credit: Brandi Eide)

providing a means for patterning molecular linkers with attachment points to catalytic complexes (Fig. 1). The modular aspect of this method allows independent modification of the light absorber, bridging material, anchoring functionality, or catalyst as new materials and discoveries emerge. Although a number of scientific challenges remain, the systems set the stage for a better understanding of the relationship between catalyst placement, band edges and the resulting surface potential profile at the interface.

References.

1. Lewis, N. S.; Nocera, D. G. *Proc. Natl. Acad. Sci. U.S.A.* **103**, 15729-15735 (2006).
2. Faunce, T. A.; Lubitz, W.; Rutherford, A. W.; MacFarlane D.; Moore, G. F.; Yang, P.; Nocera, D. G.; Moore, T. A.; Gregory, D. H.; Fukuzumi, S.; et al. *Energy Environ. Sci.* **6**, 695-698 (2013).
3. Moore, G. F.; Brudvig, G. W. *Annu. Rev. Condens. Matter Phys.* **2**, 303-327 (2011).
4. Blankenship, R. E.; Tiede, D. M.; Barber, J.; Brudvig, G. W.; Fleming, G.; Ghirardi, M.; Gunner, M. R.; Junge, W.; Kramer, D. M.; Melis, A.; et al. *Science*, **332**, 805-809 (2011).
5. Hammarström, L.; Winkler, J. R.; Gray, H. B.; Styring, S. *Science* **333**, 288 (2011).
6. Moore G. F.; Sharp, I. D. *J. Phys. Chem. Lett.* **4**, 568-572 (2013).

A Molecular Solution to Solar Fuels

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Sunlight is intermittent, losing its ability to generate power at night. In order for the sun to serve as a primary energy source will require energy storage on massive scales - at levels that exceed the ability of existing energy storage technologies. The only realistic alternative is energy stored in chemical bonds with the energy of the sun used to carry out chemical transformations that produce "solar fuels". Photosynthesis in green plants offers a role-model but is amazingly complex built over eons, and occurs with low solar efficiencies toward biomass production.

Our target is far simpler, directed at high efficiency, low cost approaches to solar fuels based on photoelectrochemistry. The targets are water splitting into hydrogen and oxygen ($2H_2O$ Ÿ $O_2 + 2H_2$) or reduction of carbon dioxide to carbon monoxide, other oxygenates, such as methanol, or even better, liquid hydrocarbons. Our research is based on Dye Sensitized Photoelectrosynthesis Cells (DSPEC). In these devices water splitting occurs at a photoanode and CO_2 or water reduction at a cathode or photocathode.[1, 2]

DSPECs rely on molecules "to do the work."[1,2] Chromophore-catalyst assemblies are tethered to high surface area, high band gap metal oxide semiconductors. The assemblies absorb light, inject electrons into the semiconductor, steer electron flow, and catalyze the solar fuel half reactions - water oxidation and water or carbon dioxide reduction. Achieving adequate solar efficiencies depends on absorbing a high fraction of the solar spectrum and mastering interfacial dynamics for electron transfer and catalysis in a stabilized interfacial architecture.

The DSPEC strategy relies on a "modular approach" with fully integrated research teams focusing on the different elements in an overall device. Molecular assemblies for light absorption and catalysis are at the heart of the strategy and we have developed multiple targets, initially, building on the extensive and impressive background synthetic, photochemical, and catalytic chemistry available for Ru polypyridyl complexes.

An initial breakthrough came with "green dimer" assemblies, $[(bpy)_2Ru^{II}(bpm)Ru^{II}(tpy)(OH_2)]^{4+}$ and $[(bpy)_2Ru^{II}(bpm)Ru^{II}$ Mebimpy)$(OH_2)]^{4+}$ (**(1)**: bpy=2,2'-bipyridine; bpm=2,2'-bipyrimidine; tpy=2,2':6',2"-terpyridine; Mebimpy: 2,6-bis(1-methyl-benzimidazol-2-yl)pyridine).[3] They proved to be stable, robust, efficient water oxidation catalysts either in solution or, as the phosphonate derivatives shown in Figure 1, tethered to the surfaces of tin-doped indium oxide (ITO) or fluoride-doped tin oxide (FTO) electrodes. Surface-bound assembly **(1)** was shown to undergo 28,000 water oxidation turnovers over a 13 h electrolysis period with Faradaic efficiencies as high as 98% with no loss in catalytic activity.

Although effective as electrocatalysts for water oxidation, the green dimers have relatively low electron injection efficiencies on TiO_2. The lowest-lying metal-to-ligand charge transfer (MLCT) excited states are localized on the bridging ligand between the chromophore and catalyst away from the semiconductor interface. Visible light absorption to the bridging ligand, which dominates in the low energy visible, results in limited or no injection.

Injection efficiencies from the chromophore in the assembly $[((PO_3H_2\text{-}CH_2)\text{-}bpy)_2Ru_a(bpy\text{-}NH\text{-}CO\text{-}trpy)Ru_b(bpy)(OH_2)]^{4+}$ (**(2)**: $((PO_3H_2\text{-}CH_2)_2$-bpy = ([2,2**Nj** -bipyridine]-4,4**Nj** -diylbis-(methylene))diphosphonic acid); bpy-ph-NH-CO-trpy = 4-([2,2**Nj**:6**Nj**,2**nj** -terpyridin]-4**Nj**-yl)-*N*-((4**Nj**-methyl-[2,2**Nj**-bipyridin]-4-yl)- methyl) benzamide); bpy = 2,2**Nj**-bipyridine), on TiO_2 are ~1 in acidic solution. Injection is followed by 140-150 ps intra-assembly electron transfer, [TiO$_2$(e$^-$)**ī** Ru$_a^{III}$**ī** Ru$_b^{II}$**ī** OH$_2$]$^{5+}$ Ÿ [TiO$_2$(e$^-$)**ī** Ru$_a^{II}$**ī** Ru$_b^{III}$**ī** OH$_2$]$^{5+}$. Back electron transfer, [TiO$_2$(e$^-$)**ī** Ru$_a^{II}$**ī** Ru$_b^{III}$**ī** OH$_2$]$^{5+}$Ÿ [TiO$_2$**ī** Ru$_a^{II}$**ī** Ru$_b^{II}$**ī** OH$_2$]$^{4+}$, occurs on the microseconds-milliseconds timescale.[4]

In assembly **(3)**, Figure 1, the monomeric precursor, $[Ru(tpy)(Mebim\text{-}py)(OH_2)]^{2+}$ (Mebim-py = 2-pyridyl-*N*-methyl-benzimidazole), is a facile water oxidation catalyst.[5] The rate of water oxidation in solution with added Ce(IV) is increased by a factor of ~8 when using the non-phosphonated assembly $[(bpy)_2Ru($4-Mebpy-4**Nj** bimpy$)Ru(tpy)(OH_2)]^{4+}$. The rate enhancement was attributed to an

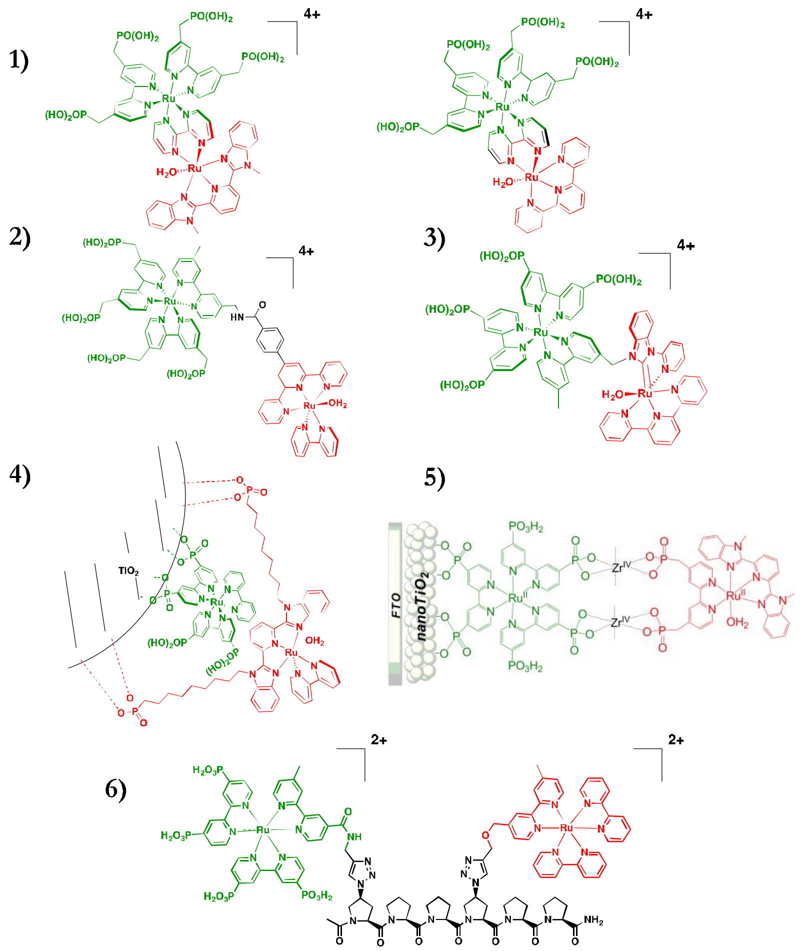

Figure 1. Chromophore-catalyst structures: 1) green dimers; 2) amide-coupled; 3) methylene bridge; 4) overlayer; 5) layer-by-layer 6) oligoproline molecular antenna.

internal catalytic effect induced by the rapid electron transfer characteristics of the chromophore.[5] In current experiments, assembly **(3)** is under investigation in a DSPEC for light-driven water splitting.

In assembly **(4)**, an "overlayer" strategy was adopted. The assembly was prepared on ITO by a stepwise procedure. In the first step, ITO was derivatized with the ruthenium chromophore $[Ru(bpy)(4,4'-(PO_3H_2bpy)_2)]^{2+}$. The catalyst, $[Ru(bpy)(P_2Mebim_2py)OH_2]^{2+}$ (P_2Mebim_2py = 2,6-bis[1-(10-diethylphosphonyl)decylbenzimidazol-2-yl]pyridine), with the benzimidazol ligand derivatized with long tail $-(CH_2)_9-PO_3H_2$ substituents, was then added as an overlayer (Figure 1).[6] With no requirement for a chromophore-catalyst link, this is a synthetically appealing, straightforward way to prepare surface assemblies by sequential dipping. However, catalytic water oxidation was not sustained. Upon water oxidation and O_2 release, the open coordination site on the metal appears to bind to the phosphonate group of one of the long tails blocking the site to further water addition.

We have also developed a "layer-by-layer" approach to give assembly **(5)** which also greatly simplifies synthesis. This approach is based on phosphonate/Zr^{4+}/phosphonate coordination and bridging, note the assembly structure **(5)** in Figure 1. With this approach, the desired assembly is also accessible by simple dipping methods without a need for covalent bond formation. Transient absorption measurements show that following injection, rapid through-assembly electron transfer occurs from the external catalyst to the oxidized chromophore at the interface beginning the process of oxidative activation.[7]

The most flexible covalent approach to assemblies has come from exploitation of the step-by-step procedure used in solid state peptide synthesis. In this procedure the desired elements are assembled stepwise on a derivatized polystyrene bead followed by cleavage from the bead. This provides spatial control of the components and, with it, an element of control of intra-assembly electron and energy transfer. Oligoprolines are especially attractive in this application given their tendency to form spatially defined polyproline helices and with it, control of electron and energy transfer distances, note assembly **(6)** in Figure 1. In **(6)** on nanoparticle films of ZrO_2, time-dependent energy transfer was observed and time-resolved from the outer to the inner chromophore demonstrating an assembly antenna effect. On TiO_2, excitation and injection by the inner chromophore was followed by rapid intra-assembly electron transfer.[8] Studies with multiple chromophores and a family of chromophore-catalyst assemblies are currently under investigation.

The UNC EFRC is moving ahead rapidly in its mission of utilizing DSPEC and related architectures for Artificial Photosynthesis and Solar Fuels. Underpinning these efforts has been an impressive development of multiple synthetic strategies which yield key molecular assemblies that are now being explored in device configurations. Stay tuned, the best is yet to come.

References.

1. Alibabaei, L.; Luo, H.; House, R. L.; Hoertz, P. G.; Lopez, R.Meyer, T. J., *Journal of Materials Chemistry A.* **Accepted**, (2013).
2. House, R. L.; Alibabaei, L.; Bonino, C.; Hoertz, P. G.; Trainham, J.Meyer, T. J., *PV Magazine.* (March, 2013).
3. Concepcion, J. J.; Jurss, J. W.; Hoertz, P. G.Meyer, T. J., *Angew. Chem. Int. Ed.* **48**, 9473-9476 (2009).
4. Ashford, D. L.; Song, W. J.; Concepcion, J. J.; Glasson, C. R. K.; Brennaman, M. K.; Norris, M. R.; Fang, Z.; Templeton, J. L.Meyer, T. J., *J. Am. Chem. Soc.* **134**, 19189-19198 (2012).
5. Norris, M. R.; Concepcion, J. J.; Harrison, D. P.; Binstead, R. A.; Ashford, D. L.; Fang, Z.; Templeton, J. L.Meyer, T. J., *J. Am. Chem. Soc.* **135**, 2080-2083 (2013).
6. Glasson, C. R. K.; Song, W. J.; Ashford, D. L.; Vannucci, A.; Chen, Z. F.; Concepcion, J. J.; Holland, P. L.Meyer, T. J., *Inorg. Chem.* **51**, 8637-8639 (2012).
7. Hanson, K.; Torelli, D. A.; Vannucci, A. K.; Brennaman, M. K.; Luo, H. L.; Alibabaei, L.; Song, W. J.; Ashford, D. L.; Norris, M. R.; Glasson, C. R. K.; Concepcion, J. J.Meyer, T. J., *Angew. Chem. Int. Ed.* **51**, 12782-12785 (2012).
8. Ma, D.; Bettis, S. E.; Hanson, K.; Minakova, M.; Alibabaei, L.; Fondrie, W.; Ryan, D. M.; Papoian, G. A.; Meyer, T. J.; Waters, M. L.Papanikolas, J. M., *J. Am. Chem. Soc.* **135**, 5250-5253 (2013).

One approach to artificial photosynthesis

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Research in artificial photosynthesis includes experiments designed to elucidate the fundamental principles governing natural photosynthesis and their application to the design of synthetic solar energy conversion systems. Artificial systems are not intended to exactly reproduce the natural process, but rather to adapt its basic principles in order to achieve the production of fuel or electricity with improved efficiency[1-5]. As in natural photosynthesis, an artificial reaction center for solar fuel production should absorb light in the visible and near-infrared regions of the solar spectrum, generate a charge-separated state, spatially separate and stabilize the charges and transport the photo-generated oxidizing and reducing equivalents to catalysts which carry out the chemical reactions necessary for the production of a fuel (e.g., production of H2 by electrons obtained from the oxidation of water). Much of the research of the Gust, Moore, and Moore (GMM) group has been centered on the development and study of artificial reaction centers with the dual objectives of reaching a better understanding of photosynthesis and developing bio-inspired solar-to-fuel systems[6-9]. In the work outlined below, several examples from the GMM group are used to illustrate the research trajectory aimed at this ultimate goal.

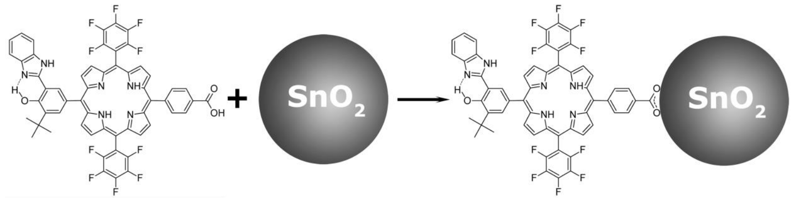
Since the late 1970s myriad approaches to the design of artificial reaction centers have been reported[10-12]. Covalently linking two molecular analogs of the cofactors involved in the photosynthetic reaction center (e.g., chlorophylls, porphyrins, phthalocyanines, carotenoids, pheophytins, quinones) produced some of the simplest artificial reaction centers. Early work in the field demonstrated that porphyrin–quinone (P–Q) dyads could form the $P^{\bullet+}$– $Q^{\bullet-}$ charge-separated state upon excitation of the porphyrin[13-14]. However, the extremely fast decay of this state (on the sub-nanosecond time scale) by charge recombination made it difficult to imagine coupling the photo-generated redox potential in $P^{\bullet+}$– $Q^{\bullet-}$ directly to slower catalytic steps to yield energy-rich products. In the natural system, sequential electron transfer steps following photo-induced charge separation spatially separates positive and negative charges across a substantial distance, which greatly slows recombination. Following this design principle, incorporating a third component thermodynamically capable of carrying out a second electron transfer after the initial photo-induced charge separation has proven essential for extending the lifetime of the charge-separated state.

In the early 1980s[15-16] Gust, Moore and Moore designed and synthesized a series of carotenoid–porphyrin (CĪ P) dyads and concluded from electrochemical and pulse radiolysis studies that a radical cation generated on the porphyrin moiety ($P^{\bullet+}$) of this dyad would migrate to form the $C^{\bullet+}$–P species[17]. Combining this observation with reports of the formation of $P^{\bullet+}$–$Q^{\bullet-}$ species by photo-induced electron transfer in P–Q dyads led to the design, synthesis, and subsequent study of photo-induced electron transfer processes in a carotenoid–porphyrin–quinone (C–P–Q) triad[18-19]. Transient spectroscopic studies of C–P–Q showed that illumination with visible light (~600 nm) generated the porphyrin first excited singlet state, C–^{1}P–Q, which decayed by photo-induced charge transfer to the first charge-separated state, C–$P^{\bullet+}$–$Q^{\bullet-}$. Competing with recombination, a second electron transfer, from the carotenoid to the porphyrin radical cation (predicted from previous work on C–P dyads) produced the final charge-separated state $C^{\bullet+}$–P–$Q^{\bullet-}$ with a much longer lifetime of 170 ns in dichloromethane, increasing to 2.5 μs in electrolyte-saturated solvent[18]. The triad marked a major improvement in stabilizing charge separation in an artificial reaction center by demonstrating that a series of short-range, fast, high quantum yield electron transfer reactions could result in long-lived charge separated states. Earlier work by Marcus and others provided the theoretical foundation for this strategy, which is used in natural and artificial reaction centers: the short-range, fast electron transfer steps are near the maximum (ī æG^0 = λ) of the Marcus curve, whereas charge recombination is located deeply in the inverted region (ī æG^0 > λ) and is therefore slow, resulting in high quantum yields of long-lived charge separated states[20]. The observations made on the original triad have proven to be universal and have been extended to more complex multiple component systems[6-7], [21-24]. Thus, the triad system established a platform for engineering efficient artificial reaction centers that were used in more complex systems in order to study other processes related to photosynthesis[25-26].

Recently, with photosystem II (PSII) from water-oxidizing photosynthesis in mind, we constructed a triad consisting of a tetracyanoporphyrin (TCNP) electron acceptor covalently-linked to a high-potential porphyrin bearing two pentafluorophenyl groups (PF_{10}) that acts as the primary electron donor. The PF_{10} in turn is connected to a benzimidazole-phenol (Biī PhOH) component that acts as a secondary electron donor27. In this construct, PF10 is a model of P680, the initial chlorophyll electron donor of PSII, and Biī PhOH mimics the tyrosine-histidine (Yz–His190) redox relay that is involved in shuttling electrons between P680 and the oxygen evolving complex (OEC), which is the catalytic site of water oxidation in PSII. As with the Yz–His190 pair, the electron transfer reaction involving the Biī PhOH unit in the triad features an associated proton transfer process (PCET).

Excitation of the PF10 component in benzonitrile is followed by singlet energy transfer to the TCNP unit, whose excited state decays by photo-induced electron transfer to yield the Biī PhOHī $PF_{10}^{\bullet+}$ī $TCNP^{\bullet ī}$ intermediate charge separated state. A second electron transfer reaction from the Biī PhOH to the PF_{10} radical cation follows, giving a final state postulated as BiH^+ī $PhO^{\bullet}$ī PF_{10}ī $TCNP^{\bullet ī}$, in which the phenolic proton now resides on the benzimidazole moiety. This final state decays with a time constant of 3.8 εs.

Coupling an artificial reaction center to water oxidizing catalysts presents two obvious challenges. First, the catalyst may not operate on the fast timescale of the primary electron and hole transfers in the reaction center and second, the high oxidation potential necessary for water oxidation must be preserved. To address these challenges in a construct that sets the stage for incorporation of the artificial reaction center discussed above into a transparent nanoparticulate wide band gap semiconductor photoanode[5, 28], a molecular dyad consisting of Biī PhOH and PF10 subunits has been attached to 2.5 nm SnO_2 semiconducting nanoparticles (NPSnO_2) using a meso-(4-carboxyphenyl) functionality on the PF$_{10}$ unit as a linker to the metal oxide (Scheme 1). Attachment of the molecular dyad to the SnO_2 was carried out in methanol at 50ºC under continuous stirring for 24 h, as described elsewhere for metal oxide functionalization[29]. Briefly, the crude Biī PhOHī PF$_{10}$ī NPSnO_2 construct was dried under reduced pressure, dissolved in water, and washed several times with dichloromethane in order to remove unattached dyads. The Biī PhOHī PF$_{10}$–NPSnO_2 complex remained in the aqueous phase, while the unattached Biī PhOHī PF$_{10}$ dyad was transferred to the organic phase.



Scheme 1. Attachment of Biī PhOHī PF$_{10}$ to NPSnO_2 (nanoparticle is not to scale).

Time-resolved transient absorption measurements in the nanosecond to millisecond time-range were performed in order to detect the generation of the BiH$^+$ī PhO$^\bullet$ī PF$_{10}$–NPSnO_2(e–) charge separated state. Figure 1 shows the transient absorption data in aqueous solution at pH 7. Global analysis of the data yielded evolution associated difference spectra (EADS)[30] with decay components of 2 μs, 93 μs and 33 ms. The 2 μs EADS (open squares) is mostly associated with the triplet excited state of the PF$_{10}$ (presumably resulting from dyads physisorbed to the NPSnO_2)[31] showing ground state bleaching at 420 nm (Soret band) and induced absorption around 460 nm and 750 nm[32-33]. The 93 μs EADS (solid circles) can be associated with decay of BiH$^+$ī PhO$^\bullet$ī PF$_{10}$–NPSnO_2(e–) because there is no ground state bleaching of PF$_{10}$. The induced absorption around 400 nm is associated with PhO$^\bullet$ [27] and the broad absorption from 600 nm to 1000 nm is associated with the NPSnO_2(e–), confirming the successful formation of the expected final charge separated state. The 33 ms EADS can be assigned to a mixture of several species including possible contributions from BiH$^+$ī PhO$^•$ī PF$_{10}$–NPSnO$_2$(e–) (the dyad–NPSnO$_2$ construct is expected to be heterogeneous and to have multiple decay times; see inset in Figure 1) and/or BiH$^+$ī PhO$^•$ī PF$_{10}$ formed from BiH$^+$ī PhO$^•$ī PF$_{10}$–NPSnO$_2$(e–) by loss of the dyad radical from the NPSnO$_2$. The neutral phenoxyl radical PhO$^•$ indicated by the induced absorption around 400 nm in the 33 ms EADS is attributed to such a species[27]

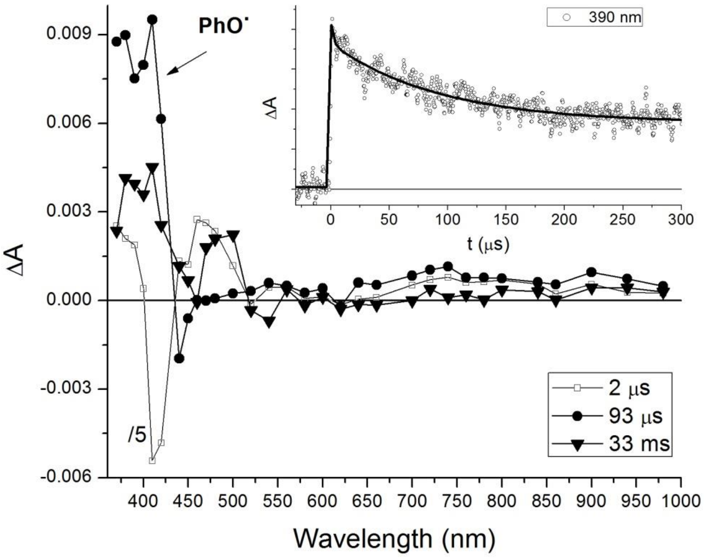


Figure 1. Evolution associated difference spectra (EADS) of Bi-PhOH-PF$_{10}$-NPSnO$_2$ nano-assemblies in air-saturated water solution at pH 7 measured by flash-photolysis (ns to μs range) upon excitation at 440 nm. Inset: Kinetic trace (open points) and fitting (line) at 390 nm.

. Electron transfers between BiH$^+$ī PhO$^•$ī PF10–NPSnO$_2$(e–) and other particles containing SnO$_2$ and the dyad could also occur on this time scale, and lead to separated radicals and ions with long lifetimes. The absorption around 480 nm and the ground state bleaching around 520 and 650 nm are not assigned, but do indicate the presence of porphyrin-based radical species that could arise in the physisorbed, aggregated dyads. In summary, the transient work shows that irradiation of the dyad-bearing nanoparticles yields BiH^{+}ī PhO$^{•}$ī PF$_{10}$–NPSnO$_2$(e–), which decays by a variety of pathways.

In this short essay, we have briefly described a few steps in the evolution of our work from early designs of artificial reaction centers containing only organic chromophores to one of our most recent models, a hybrid triad consisting of a molecular dyad attached to a semiconductor nanoparticle, thus comprised of both organic and inorganic materials. This bio-inspired construct is able to undergo sequential photo-induced electron transfer reactions and an associated proton transfer process that yield a final long lived charge separated state characterized by an electron in the semiconducting SnO$_2$ nanoparticle and a neutral phenoxyl radical. The long lifetime (93 εs) of this state should facilitate the coupling of its high oxidation potential to the relatively slow steps of water oxidation by a suitable catalyst. This bio-inspired construct highlights the possibility of using such hybrid organic-inorganic constructs in photo-conversion devices.

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References

1. Lewis, N. S.; Nocera, D. G. *Proc. Natl. Acad. Sci. U.S.A.* **103**, 15729-15735 (2006).

2. Faunce, T. A.; Lubitz, W.; Rutherford, A. W.; MacFarlane D.; Moore, G. F.; Yang, P.; Nocera, D. G.; Moore, T. A.; Gregory, D. H.; Fukuzumi, S.; et al. *Energy Environ. Sci.* **6**, 695-698 (2013).

3. Moore, G. F.; Brudvig, G. W. *Annu. Rev. Condens. Matter Phys.* **2**, 303-327 (2011).

4. Blankenship, R. E.; Tiede, D. M.; Barber, J.; Brudvig, G. W.; Fleming, G.; Ghirardi, M.; Gunner, M. R.; Junge, W.; Kramer, D. M.; Melis, A.; et al. *Science*, **332**, 805-809 (2011).

5. Hammarström, L.; Winkler, J. R.; Gray, H. B.; Styring, S. *Science* **333**, 288 (2011).

6. Moore G. F.; Sharp, I. D. *J. Phys. Chem. Lett.* **4**, 568-572 (2013).

7. Gust, D.; Moore, T. A.; Moore, A. L. *Acc. Chem. Res.* 2000, 34, 40-48.

8. Kodis, G.; Herrero, C.; Palacios, R.; Mariño-Ochoa, E.; Gould, S.; de la Garza, L.; van Grondelle, R.; Gust, D.; Moore, T. A.; Moore, A. L.; Kennis, J. T. M., *J. Phys. Chem.* B 2003, **108**, 414-425.

9. Terazono, Y.; Moore, T. A.; Moore, A. L.; Gust, D., Light harvesting, excitation energy/electron transfer, and photoregulation in artificial photosynthetic systems. In Multiporphyrin Arrays, Kim, D., Ed. Pan Standford Publishing: 2012; pp 349-387.

10. Gust, D.; Moore, T. A., Electron Transfer in Model Systems for Photosynthesis. In Photoinduced Charge Separation and Energy Migration in Supramolecular Species, Balzani, V., Ed. D. Reidel Press: Boston, 1987; pp 267-282.

11. Moore, T. A.; Gust, D., Charge Separation in Model Compounds for Photosynthesis. In Proceedings, Protein Structure: Molecular and Electronic Reactivity Conference, Austin, R.; Buhks, E.; Chance, B.; DeVault, D.; Dutton, P. L.; Fravenfelder, H.; Gol'damskii, V. I., Eds. Springer-Verlag: New York, 1987; pp 389-398.

12. Gust, D.; Moore, T. A.; Moore, A. L., *Farad. Discuss.* 2012, **155**, 9-26.

13. Tabushi, I.; Koga, N.; Yanagita, M., *Tetrahedron Lett.* 1979, **20**, 257-260.

14. Kong, J. L. Y.; Loach, P. A. *J. Heterocyclic Chem.* 1980, **17**, 737-744.

15. Bensasson, R. V.; Land, E. J.; Moore, A. L.; Crouch, R. L.; Dirks, G.; Moore, T. A.; Gust, D., *Nature* 1981, **290**, 329-332.

16. Moore, A. L.; Joy, A.; Tom, R.; Gust, D.; Moore, T. A.; Bensasson, R. V.; Land, E. J., *Science* 1982, **216**, 982-984.

17. Land, E. J.; Lexa, D.; Bensasson, R. V.; Gust, D.; Moore, T. A.; Moore, A. L.; Liddell, P. A.; Nemeth, G. A., *J. Phys. Chem.* 1987, **91**, 4831-4835.
18. Moore, T. A.; Gust, D.; Mathis, P.; Mialocq, J.-C.; Chachaty, C.; Bensasson, R. V.; Land, E. J.; Doizi, D.; Liddell, P. A.; Lehman, W. R.; Nemeth, G. A.; Moore, A. L., *Nature* 1984, **307**, 630-632.
19. Gust, D.; Moore, T. A., *Science* 1989, **244**, 35-41.
20. Marcus, R. A., *Angew. Chem. Int. Ed.* 1993, **32**, 1111-1121.
21. Gust, D.; Moore, T. A.; Moore, A. L.; Barrett, D.; Harding, L. O.; Makings, L. R.; Liddell, P. A.; De Schryver, F. C.; Van der Auweraer, M.; et al., *J. Am. Chem. Soc.* 1988, **110**, 321-323.
22. Gust, D.; Moore, T. A.; Moore, A. L.; Lee, S. J.; Bittersmann, E.; Luttrull, D. K.; Rehms, A. A.; Degraziano, J. M.; Ma, X. C.; Gao, F.; Belford, R. E.; Trier, T. T., *Science* 1990, **248**, 199-201.
23. Kodis, G.; Liddell, P. A.; Moore, A. L.; Moore, T. A.; Gust, D., *J. Phys. Org. Chem.* 2004, **17**, 724-734.
24. Kodis, G.; Liddell, P. A.; de la Garza, L.; Clausen, P. C.; Lindsey, J. S.; Moore, A. L.; Moore, T. A.; Gust, D., *J. Phys. Chem.* A 2002, **106**, 2036-2048.
25. Steinberg-Yfrach, G.; Liddell, P. A.; Hung, S.-C.; Moore, A. L.; Gust, D.; Moore, T. A., *Nature* 1997, **385**, 239-241.
26. Steinberg-Yfrach, G.; Rigaud, J.-L.; Durantini, E. N.; Moore, A. L.; Gust, D.; Moore, T. A., *Nature* 1998, **392**, 479-482.
27. Megiatto, J. D.; Antoniuk-Pablant, A.; Sherman, B. D.; Kodis, G.; Gervaldo, M.; Moore, T. A.; Moore, A. L.; Gust, D., *Proc. Natl. Acad. Sci. U.S.A.* 2012.
28. O'Regan, B.; Grätzel, M., *Nature* 1991, **353**, 737-740.
29. Llansola-Portoles, M. J.; Bergkamp, J. J.; Tomlin, J.; Moore, T. A.; Kodis, G.; Moore, A. L.; Cosa, G.; Palacios, R. E., *Photochem. Photobiol.* 2013, *in press*.
30. van Stokkum, I. H. M.; Larsen, D. S.; van Grondelle, R., *Bioch. Biophys. Acta* 2004, **1657**, 82-104.
31. Hernandez, L. I.; Godin, R. P.; Bergkamp, J. J.; Llansola-Portoles, M. J.; Sherman, B. D.; Tomlin, J.; Kodis, G.; Méndez-Hernández, D. D.; Bertolotti, S.; Chesta, C.; Mariño-Ochoa, E.; Moore, A. L.; Moore, T. A.; Cosa, G.; Palacios, R. E., *J. Phys. Chem. B* 2013, *117*, 4568-4581.
32. Luo, C.; Guldi, D. M.; Imahori, H.; Tamaki, K.; Sakata, Y., *J. Am. Chem. Soc.* 2000, **122**, 6535-6551.
33. Gouterman, M., J. Molec. J. Mol. Spectrosc. 1961, **6**, 138-163.

On a dispute between Ciamician and Paternò

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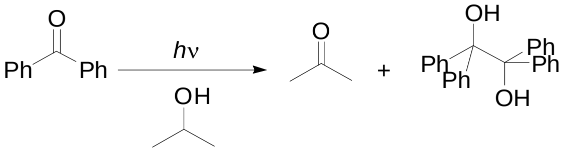
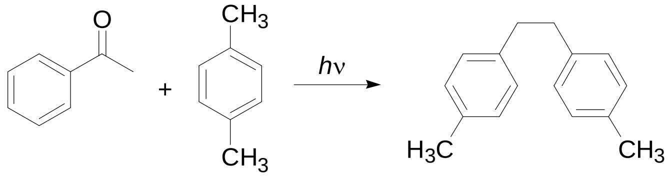
In the last article of the series "Synthesis in organic chemistry by means of light" Paternò launched a violent attack toward Giacomo Ciamician.[1] Ciamician and Silber, studying the photochemical behaviour of alcohols in the presence of aldehydes and ketones, showed that an oxidation reaction occurred on the alcohol (Scheme 1).[2]



Scheme 1

When this reaction has been performed irradiating benzophenone in the presence of cymene, they observed the formation of the oxidation product of benzophenone, but they could not identify the transformation product of *p*-cymene.[3] Paternò, in a communication at the Accademia Nazionale dei Lincei performed during 1908 (and published in the subsequent year)[4] and in the conference at London in 1909 and whose test we have partially reproduced in the previous issue of this letter,[5] showed that *p*-xylene gave the dimeric product 1,2-(4-methyl-1-phenyl)-ethane (Scheme 2).[6] He did not identify the product obtained by using *p*-cymene. Ciamician, several months after this communication, published an article where the dimeric nature of the irradiation product of *p*-cymene was clarified.[7] Paternò claimed the priority on this reaction noting that Ciamician hastened to remake previous experiments, where he was not able to identify the product.

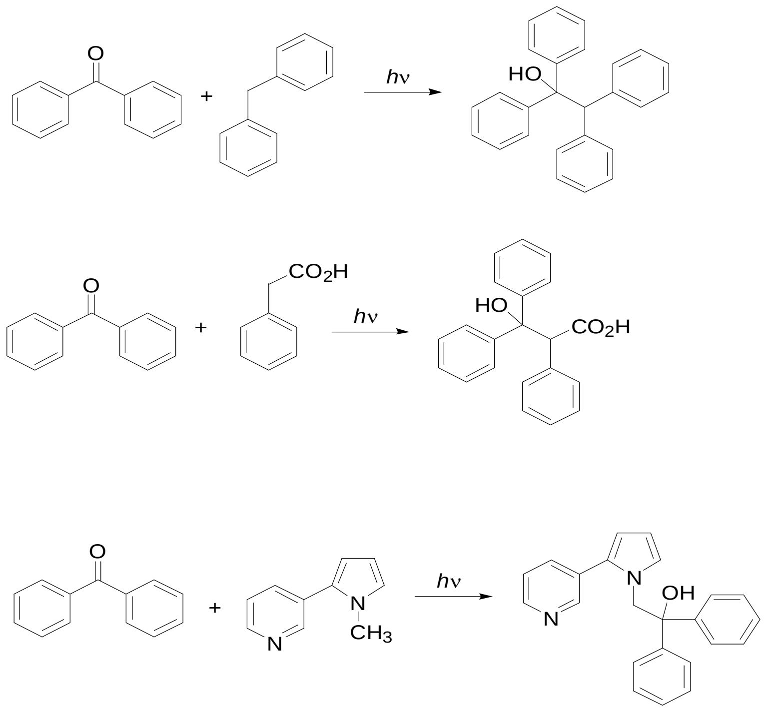


Scheme 2

Ciamician replied to this charge showing that Paternò was not able to identify the product obtained during the irradiation of *p*-cymene, and that he decided to reconsider this reaction after the work of Paternò.[8]

Furthermore, some other reactions will be object of this rancorous controversy between Paternò and Ciamician. Paternò showed that the irradiation of aromatic aldehydes or ketones in the presence of benzylic substrates could give a coupling reaction with the formation of the products described in the Scheme 3.[6,9,10] Some new application of this reaction appeared also in the conference report published in the last issue of EPA Newsletter.[5] In particular, he showed the reaction of acetophenone with benzyl alcohol to give 1,2-diphenyl-1,2-propanediol.[10] Ciamician noted[11] that in 1903 he reported the reaction between benzophenone and benzyl alcohol.[12] Paternò, on the other hand, noted[1] that in that article the authors were not sure on the identification of the product, and that, after his work, Ciamician had repeated his experiments, adding few new results.[13] Ciamician replied that, in a full paper on the Gazzetta Chimica Italiana, he reported the complete identification of the product.[8]

We could add some other examples of this controversy, but I think it is not useful. It is evident the complex relationship between these two characters. It is evident they are in competition. Undoubtedly, Ciamician was right when he complained that Paternò was entered in the field of photochemistry without any respect for him.[8] On the other hand, the period of this controversy corresponds to the death of Stanislao Cannizzaro (1910), the men that had in his hands all the destiny of the chemistry in Italy. Paternò and Ciamician are both senators and they aspired to the role of Cannizzaro. The contraposition between these two characters was not avoidable. And probably, now we are able to affirm that Paternò was the winner in this competition.



Scheme 3

References

1. Paternò, E. *Gazz. Chim. Ital.* **44**(II), 463-475 (1914).
2. Ciamician, G.; Silber, P. *Ber. Dtsch. Chem. Ges.* **33**, 2911(1900); Ciamician, G.; Silber, P. *Ber. Dtsch. Chem. Ges.* **34**, 1530 (1901).
3. Ciamician, G.; Silber, P. *Gazz. Chim. Ital.* **34**(II), 135 (1904).
4. Paternò, E. *R. Accad. Lincei, Rendiconti,* **18**(1), 104 (1909).
5. Paternò, E. *Rev. Gener. Chim. Pure Appl.* **12**, 299 (1909); *EPA Newsletter*, **83**, 72 (2012).
6. Paternò, E.; Chieffi, G. *Gazz. Chim. Ital.* **39**(II), 415 (1909).
7. Ciamician, G.; Silber, P. *R. Accad. Lincei, Rendiconti* **19**(I), 645 (1910).
8. Ciamician, G.; Silber, P. *R. Accad. Lincei, Rendiconti* **24**(I), 17 (1915).
9. Paternò, E.; Chieffi, G. *Gazz. Chim. Ital.*, **40**(II), 321 (1910); Paternò, E.; Forlì Forti, G. *Gazz. Chim. Ital.*, **40**(II), 332 (1910);

Paternò, E.; Maselli, C. *Gazz. Chim. Ital.*, **42**(I), 65 (1912); Paternò, E.; Chieffi, G.; Perret, G. *Gazz. Chim. Ital.*, **44**(I), 237 (1914); Paternò, E.; Chieffi, G.; de Fazi, R. *Gazz. Chim. Ital.*, **44**(II), 99 (1914).

10. Paternò, E.; Chieffi, G.; Perret, G. *Gazz. Chim. Ital.*, **44**(I), 151 (1914).

11. Ciamician, G.; Silber, P. *R. Accad. Lincei, Rendiconti* **23**(I), 112 (1914).

12. Ciamician, G.; Silber, P. *R. Accad. Lincei, Rendiconti* **12**(II), 235 (1903).

13. Ciamician, G.; Silber, P. *Ber. Dtsch. Chem. Ges.*, **43**, 945 (1910); Ciamician, G.; Silber, P. *Ber. Dtsch. Chem. Ges.*, **44**, 1554 (1911); Ciamician, G.; Silber, P. R. *Acc. Lincei*, *Rendiconti* **21**, 547 (1912).

TECHNICAL NOTES

Introducing the Solar Fuels Network

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The field of solar fuels (or "artificial photosynthesis") has witnessed a rapid expansion over the last few years. With pressing concerns about energy security and global warming, research into renewable energy forms is intense. Solar fuels offers the potential for storing the sun's energy in chemical bonds, by using sunlight to drive photo(electro)chemical water splitting or CO_2 reduction to produce H_2, methanol, formic acid, etc. Photochemistry is essential to understand and evaluate the mechanisms of light absorption, charge separation/transfer and catalysis involved in light-driven fuels synthesis.

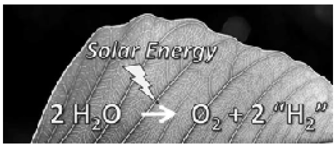

Figure 1. Light-driven fuels synthesis allows the sun's energy to be stored in chemical bonds via photo(electro)chemical water splitting and/or CO_2 reduction.

The Solar Fuels Network (SFN) is a UK-based organisation funded by the EPSRC with the purpose of developing an effective community of UK solar fuels researchers. The Network is led by Prof James Durrant (Imperial College) and the advisory board includes researchers from all areas of academic solar fuels research in the UK, as well as industry representatives. The overall aims of the Network are to: 1. raise the profile of the UK solar fuels research community nationally and internationally; 2. contribute towards the development of a UK technology and policy roadmap in solar fuels; 3. promote collaboration and co-operation between this community and other relevant research and development communities – including other research disciplines, industry and international solar fuels programmes.

In order to meet these aims, the SFN will organise and support various activities and events. This includes organisation of symposia, workshops and conferences, as well as summer/winter schools and outreach activities, and publication of a regular newsletter. Bilateral/international collaborations, and financial assistance for students to attend symposia, summer schools etc will be supported by the SFN. The Network will also organise and support outreach activities that aim to inform the public about solar fuels research and technologies.

Engagement with the public via outreach activities has great importance for three main reasons. Firstly, to raise awareness of the impact of scientific research on everyday life (energy technology, microchips, medicines, transport, climate change…). Secondly, to help recruit the next generation of scientists by enthusing children about science. Finally, research is publicly funded and the public is entitled to know about the research that is funded by their taxes.

We are currently developing various outreach activities which are suitable for a wide range of age groups and levels of scientific knowledge. Our aim is to generate a library of demonstrations and activities that can be drawn from to create solar fuels-based stalls for different public engagement events. We recently presented a stall called "Colourful Chemistry, Renewable Energy" at the second Imperial Festival.[1] On this occasion, our aim was to raise awareness of the importance of spectroscopy and photochemistry in studying materials for solar fuels. In order to cater for a wide range in age and background knowledge, we had several different activities and demonstrations on the stall. These included: extracting chlorophyll from spinach with acetone; demonstration of fluorescence from chlorophyll and laser dyes using a torch (flashlight); demonstration of the Tyndall effect using flour and water solutions and a torch; electrolysis of water using a 9V battery and two pencils as electrodes; and the reaction of H_2O_2 with Rochelle salt catalysed by $CoCl_2$ (which changes colour during the reaction). We also had samples of Fe_2O_3 and TiO_2 on FTO glass, and a collection of dye-sensitised solar cells (DSCs) with different coloured dyes which visitors could handle. We created diagrams to explain the science behind the experiments. The stall attracted a lot of interest; people (adults as well as children) got involved in the demonstrations, and many adults were particularly interested in learning more about solar fuel technologies.

Figure 2. Part of the Colourful Chemistry, Renewable Energy stall at the Imperial Festival.

Taking part in such public engagement events is highly rewarding for those involved, and raises the profile research areas that currently have low public awareness. For example, almost everyone is familiar with the concept of photovoltaic cells that generate electricity from sunlight, but very few members of the public are aware of solar fuel technologies.

The activities and demonstrations for such outreach events can be created using a very small budget, especially if some items are borrowed from the lab. Having taken part in a few such events over the last year, we can offer the following tips for a successful stall. Firstly, the RSC book "Classic Chemistry Demonstrations: One Hundred Tried and Tested Experiments"[2] is very useful. There are also many online resources available, such as those developed by The Solar Spark.[3] Secondly, having a relatively big, interesting item is very effective for drawing people in. For example, the hotplate, tubing and glassware with coloured liquid required for the $CoCl_2$-catalysed reaction was surprisingly effective for this. Thirdly, the public – especially children – generally find "hands on" activities that they can take part in more interesting than a demonstration. Chlorophyll extraction is a good example of this, as is making DSCs using the juice from fruit and vegetables. Children particularly enjoy wearing safety specs and lab coats; it makes them feel like a "real scientist". It is also worth bearing in mind that gloves and lab coats may be helpful to protect the demonstrators from mess, even if not required for safety reasons! Fourthly, it is a good idea to have more than one activity/demonstration, so that children and adults with a range of background knowledge will find something interesting. Finally, adults in particular like to see something that is "real", i.e. something that is used in the lab, whether equipment or a technique. For example, adults usually want to make DSCs once it is explained that "this is what we do in the lab", even though it might at first appear to be an activity for children.

As discussed earlier, the Solar Fuels Network will organise and support many different types of event, including workshops and symposia. The first of these will be the Solar Fuels Post-Graduate Symposium at ISACS12 (Challenges in Chemical Renewable Energy) in Cambridge in September. The PG symposium will present the work of early career researchers addressing the challenge of utilising sunlight to drive the photo(electro)chemical synthesis of fuels. This will be a forum for the exchange of ideas and information of recent advancements in the development and understanding the different approaches to solar fuel production. Areas of discussion will include photoelectrochemical and bio-inspired approaches to solar fuels production, and spectroscopy of solar-to-fuel conversion systems. The symposium is free to attend; priority for attendance will be given to students and post-docs. This is an excellent opportunity for students and early career researchers to present either a talk or a poster. Registration and abstract submission are through the ISACS12 registration – oral and poster abstracts submitted for ISACS12 will also be considered for the PG symposium. For more information about the symposium, please see the ISACS12 web page.[4]

The Solar Fuels Network will have an information stand at the Solar Fuels PG Symposium and ISACS12. The Network is free to join and is open to non-UK researchers. In the meantime, for more information please contact the author (s.pendlebury@imperial.ac.uk).

References.

1. www3.imperial.ac.uk/festival
2. *Classic Chemistry Demonstrations: One Hundred Tried and Tested Experiments*, compiled by T. Lister, Royal Society of Chemistry, 1995.
3. www.thesolarspark.co.uk/experiments/
4. www.rsc.org/ConferencesAndEvents/ISACS/ISACS12/pgs.asp

Light Sources and Wavelength Discriminators

All optical spectrometry techniques rely on the measurement of radiant power. The configuration of the instrument varies based on the measurement technique: absorption, emission, luminescence or scattering. But all of those used in the UV, visible and IR employ essentially the same subcomponents, including sources and detectors of radiant power, light discriminators, optical coupling and steering devices, signal processing electronics, and data analysis and presentation software. The exact combination, their spectral range of operation and the acceptance of performance requirements are very application-specific but often include resolution, sensitivity, and detection linearity, speed of acquisition and, of course, cost.

The performance characteristics of the optical source in an instrument play a critical role in the acquisition of reliable and meaningful data. The keys are spectral characteristics, wavelength range, temporal and spatial stability, radiant flux and directionality. Sources can be separated into continuum and laser types.

Continuum sources

Continuum sources such as incandescent lamps and some arc discharge lamps emit over a relatively broad spectral range and are commonly used in spectrometry. One of the most popular lamps is the tungsten filament lamp that operates in the visible and IR spectral region (from 300 nm to the far-IR). These are available in a wide range of electrical powers, source sizes and shapes, and with an operating lifetime often up to 20,000 hours, depending on lamp type and usage. Their low cost and relatively inexpensive power supplies make them ideal sources for many absorption instruments. However, there is little or no spectral output below 300 nm and, in general, there is also a relatively low flux density, especially in the far-IR.

The main consideration in the selection of a tungsten lamp is the filament size and its color temperature. The color temperature and the tolerance on the color temperature will determine the spectral peak of the output and also the lamp life- time (Figure 1). On average, lamp life goes down as the color temperature goes up. A typical tungsten lamp has a color temperature of 2800 °C with a lamp life, operated at rated current and voltage, of 2000 hours. The same lamp with a color temperature of 3450 °C might have a rated lifetime of only 50 hours. Lamp selection is often a compromise with respect to performance.

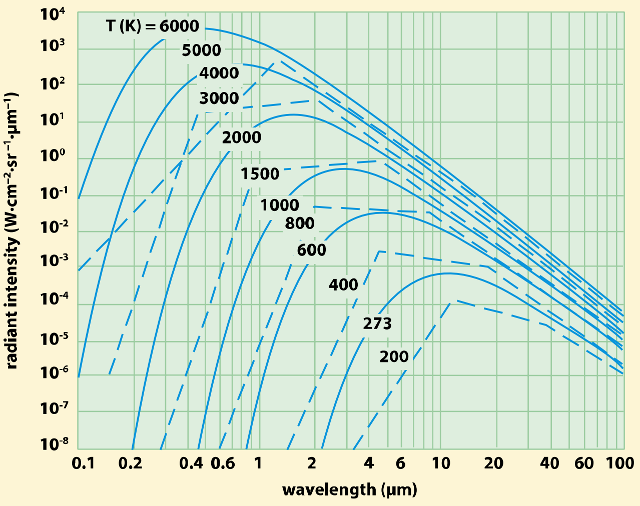

Figure 1. *Lamp output vs. color temperature for a tungsten-halogen lamp.*

Other types of incandescent continuum sources include the Nernst glower, which is an inexpensive but somewhat fragile IR source. Its life- time, like that of a tungsten lamp, depends on its operating temperature. A more rugged source is the Globar. An electrical current causes the ceramic source to heat and glow at temperatures above 1000 °C. However, cooling is needed at the electrodes, making the Globar more expensive and less convenient. Nevertheless, it offers a better emissivity than the Nernst glower at short wavelengths in the IR.

Hydrogen and deuterium arc lamps have a strong emission spectrum in the UV and can be useful from 185 nm (limited by the quartz envelope) into the visible. Shorter wavelength operation is possible by using alternate window materials such as MgF_2 , which would allow operation down to approximately 110nm. Deuterium lamps provide a higher optical output compared with hydrogen lamps (Figure 2). They are the primary light source at wave- lengths below 400 nm and are well- suited for spectroscopy because they have a relatively small arc size, have a line emission at 656 nm (essentially a built-in spectral calibration point) and have a peak spectral out- put between 220 and 230 nm. Absorption spectrometers operating in the UV and visible generally use both deuterium (200 to 350 nm) and tungsten lamps (350 to 850 nm).

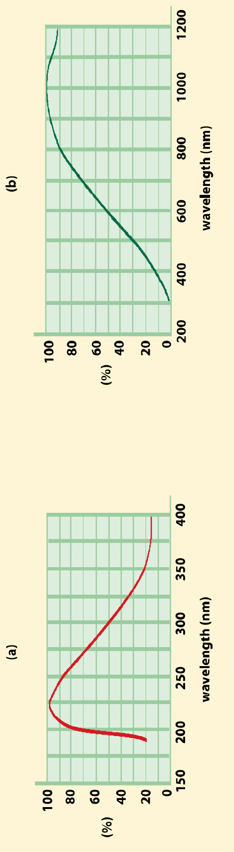

Figure 2. *Spectral output curves for (a) deuterium and (b) tungsten-halogen lamps.*

Photoluminescence instruments require high-intensity continuum sources with UV and visible output. Here, the most common source is the xenon short arc lamp, which has an intense, almost continuous spectral output from the UV (220 nm) to the near-infrared (800 nm) with some fine structure superimposed. Line spectra are prominent in the 800- to 1000-nm range, and optical output can be observed well into the IR (2.6μm). Xenon lamps have a small arc length (0.5 to 2.7 mm for 75- to 450-W lamps) and a high flux density. They are available in a variety of envelope materials allowing output from 185 nm and have relatively long operating lifetimes of up to 2000 hours.

Xenon lamps typically are operated with DC power supplies, but pulsed versions are available with 1- to 10-μs pulse widths for use in time- resolved measurements such as phosphorescence studies. Xenon lamps offer the highest flux density short of a laser. The spectral output is close to that of the sun at 6000 °C, and they make ideal solar simulators in many experiments.

Special considerations when using an arc lamp include envelope materials, ozone dissipation and convection current effects on noise, cooling, arc gap and lamp life. While they are the lamp of choice for most fluorescence instruments, these lamps require a complex power supply with an ignition circuit to strike the arc and a well-designed lamp housing to provide proper lamp cooling. They also are generally more expensive.

Line sources are used in many atomic spectrometry applications; the most common are low-pressure arc lamps such as mercury arcs. These lamps have sharp atomic line emission and are excellent sources for wavelength calibration of the spectrometer, especially in the UV. Hollow cathode lamps have become the dominant atomic spectral line source because they can produce extremely narrow atomic lines, typically with widths of 0.01 to 0.02 Å. Electrodeless discharge lamps, where a sealed envelope with a gas/metal salt mixture is placed in an intense RF or microwave field, can produce line radiances some 50 times greater than hollow cathode lamps and, until recently, because of the ready availability of lasers, have found use in fluorescence.

Lasers

Lasers are now the primary excitation source for Raman spectroscopy, but also are widely used in fluorescence and phosphorescence spectroscopy. Lasers produce discrete, narrowband, coherent wave- lengths with a sharp directionality, and are available in four main modes of operation: continuous, pulsed, Q- switched and mode-locked. All lasers rely on the ability of the systems to produce a higher number of species in the excited state than in the ground state. Once this population inversion has occurred and the lasing threshold level has been achieved, the laser will operate. Lasers offer a high flux density with high spectral monochromatic purity.

In a continuous-wave (CW) laser, the output beam is continuous in time, and the lifetime of the upper level of the lasing transition is longer than that of the lower level. The radiant power from a CW laser is from milliwatts to watts. If the upper level were to have a shorter lifetime than the lower level, then the laser would be self-terminating and could be operated only in a pulsed mode. The output from a pulsed laser occurs as either a single pulse or a train of pulses. The radiant power in a single pulse can be very high, although the average power can be quite low. The characteristics of a pulsed laser are the pulse width, the pulse energy or average power, and the repetition rate. For example, a laser producing a 10-mJ pulse in 5 ns at a repetition rate of 10Hz has a peak output of 2 MW but an average power of 0.1 W.

In a Q-switched laser, lasing is prohibited until the population inversion has reached a significantly higher value than the threshold value. The cavity is then suddenly switched on, producing a very high intensity pulse. This technique is commonly used with Nd:YAG lasers.

With a mode-locked laser, the phase of the oscillating modes are forced to correlate or be locked together. This results in a laser output that has ultrashort pulses, on the order of picoseconds or less, of very high peak power.

There are four major types of lasers:

Gas	The most common in this group are argon, helium-neon, krypton, helium-cadmium, carbon dioxide, and carbon monoxide. Excimers are a special category of gas lasers.
Diode	These offer a compact monochromatic light source. The primary wavelength of diode lasers is in the red end of the spectrum, and there are many CW and

	pulsed systems available.
Solid state	Examples are Nd:YAG and Nd:YLF lasers. If output power is sufficiently high, they can be used to pump an optical parametric oscillator (OPO), which can produce a wavelength-tunable output from visible to infrared.
Dye	These offer some flexibility in wavelength tuning at a cost in power. OPOs are replacing dye lasers in many applications.

Many specialized sources are available for specific tests: xenon flashlamps, used in the study of phosphorescence; hydrogen or nitrogen pulsed lamps, as well as ultra-high speed pulsed LEDs and Laser diodes used in the study of fluorescence lifetimes; and light-emitting diodes (LEDs), used as a light source for many applications.

Light discriminators

All of the optical spectroscopy techniques require either a means to de- liver a particular wavelength to the sample, a means to analyze light from a sample, or both delivery and analysis of a particular wavelength. Sorting out this information is a major task in the spectro-chemical measurement. Particularly important is the separation of the “true” analyte signal from all of the potentially interfering ones.

This process is, in most cases, based on wavelength discrimination, but there are many other methods that can be used to increase the selectivity of the measurement, including the use of time-resolved techniques, polarization and position sensitivity. Wavelength discrimination can be accomplished by dispersive or non-dispersive means.

Monochromators and spectrographs are the most widely used dispersive instruments. They consist of a dispersive element, such as a prism or diffraction grating, and image transfer optics, which separate a small wavelength from a polychromatic source. Detectors for monochromators are usually single-channel large area devices. Spectrographs use a fixed grating geometry to monitor a spectral range dispersed over a linear array that is made up of multiple detector elements. The manufacture of commercially available prism-based monochromators is on the decline. Grating-based monochromators and spectrographs, however, are available in a wide range of configurations for applications in the 10-nm to 20-µm range. A diffraction grating is a plane or concave element with closely spaced grooves. The grating acts as a multi- slit source when illuminated by collimated radiation. Different wavelengths are diffracted and constructively interfere at different angles. Most modern spectrometers use reflection gratings with groove densities from 75 to 3600 grooves per millimeter, de- pending on the spectral range and resolution required. Grating types are separated by their method of production — ruled or holographic. Ruled gratings are made by replicating a master grating prepared by a high- precision ruling engine. Holographic gratings are made by projecting an interference pattern onto a photoresist plate, developing this to produce the pattern. Holographic gratings have essentially perfect groove patterns, al- most perfect elimination of false lines or ghosts, and significantly improved stray light rejection compared with ruled gratings.

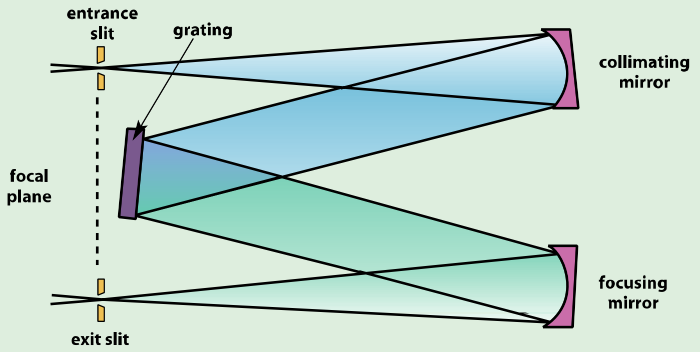

Figure 3. *The Czerny-Turner is one of the most common monochromator configurations.*

One of the most common configurations of a monochromator is the Czerny-Turner configuration (Figure 3). Many other designs are available, but most follow the same operating principle. The incident light is passed through the entrance slit and hits a collimating mirror that produces a parallel polychromatic light beam onto the diffraction grating. The grating spatially separates the spectrum in the incident light and this diffracted light is focused onto the exit slit using the focusing mirror. Each wavelength is incident upon the exit plane at a specific angle and, by rotating the grating position; one can scan these wavelengths across the exit slit and discriminate between each wavelength. The grating equation specifies the angle required to bring each wavelength through the exit slit (Figure 4),

$$n\lambda = d(\sin\alpha + \sin\beta)$$

where n is the diffraction order, d the grating groove spacing and λ the wavelength.

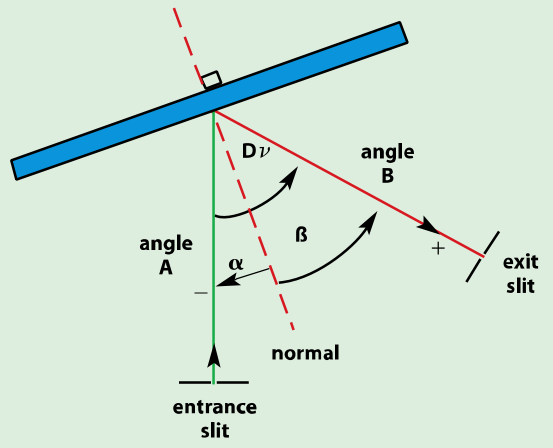

Figure 4. *Diffraction grating.*

The slits play an important role in determining the spectral resolution and throughput of the monochromator. In most cases, the slits are adjustable and can vary from a few microns to several millimeters in width. Generally the exit and en- trance slits are set to the same width.

Several characteristics are important in a monochromator, such as the linear dispersion, *f* number of solid angle, resolution, stray light rejection and throughput factors.

- The linear dispersion is how far apart spatially two wavelengths are in the focal plane, $D_L = dx/d\lambda$. The more commonly quoted figure is the reciprocal linear dispersion, $R = D^{-1} =$ $R_L = d\lambda/dx$ and represents the wavelength range within a unit distance in the focal plane.
- The limiting aperture in the instrument determines the *f* number and solid angle. Often this is the diffraction grating itself, as this is usually the most expensive element in the instrument. With a limiting aperture diameter of L, a projected area of A, and the focal length of the collimating mirror of f, the *f* number is approximately $f/\# = f/L$. The solid angle is then

$$\Omega = A/f^2 = \pi/[4(f/\#)^2]$$

- The spectral band-pass is the half-width of the wavelengthspassed across the exit slit. The bandpass is controlled by the dispersion of the monochromator except at very small slit widths where diffraction effects and aberrations need to be considered. Thus, the spectral bandpass for a given slit width, W, is $S = R_D W$.
- The resolution of the monochromator is closely related to the spectral dispersion. The dispersion governs how far apart two wavelengths are, while the resolution specifies whether the separation can be distinguished. The Rayleigh criterion states that two wavelengths, λ_1 and λ_2, are resolved if the central maxi- mum of one line falls on a diffraction minimum of the other (Figure 5). Thus, the spectral resolution can be defined by $\Delta\lambda = \bar{A}/D_a W$ where $\bar{A}$ is the average wavelength between the two lines and D the angular dispersion of the system.
- Stray light is any radiation passed by the monochromator that is out-side the selected spectral position and bandpass. In many cases, the specification of stray light is made by reference to the relative amount of radiation being passed at a spectral position defined as an

integer number of bandpass values from the test source— often a laser line. For example, a typical measurement involves filling the grating of a monochromator. Then,an intensity measurement is made both at the wavelength of the laser and at another wavelength eight band-passes away from the laser wave-length. The ratio of the latter to the former is considered the stray light of **figu** the system under this criterion. Typically, stray light is very difficult to measure, as it strongly depends upon the wavelength, bandpass used and the type of source.

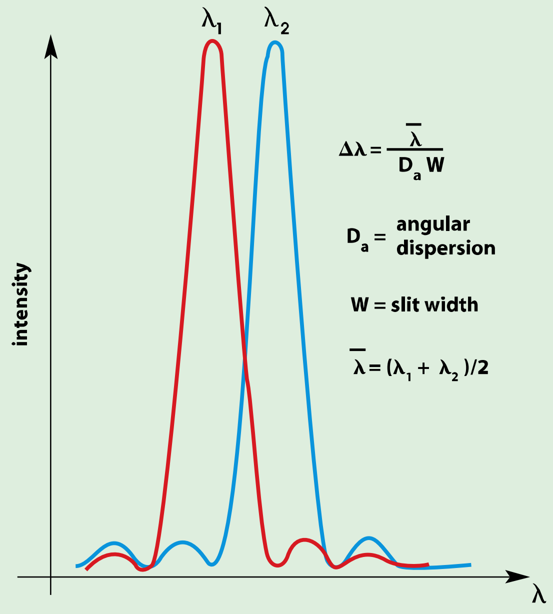

Figure 5. *Rayleigh criterion for resolution of two peaks.*

• The optical throughput of a monochromator depends upon the source, the slit height, the collected solid angle, the transmission factor of the optics and the convolution of the entrance and exit slit widths (dispersion). The light-gathering capacity (LGC) is defined by

$$LGC = \frac{height_{slit}}{(f/\#)^2 R_L}$$

Non-dispersive elements such as filters are widely used in all of the optical spectroscopy methods and re based on either absorption or interference. Filters are commercially available for wavelengths above 200 nm and come in many forms, some of which are bandpass, cut-off, heat- absorbing, heat-reflecting, etc. The most common types are:

Bandpass filters of the interference type	The bandpass wavelength and the width of the bandpass define them. It is common to use such filters to select a wavelength; i.e., excitation wavelength for fluorescence, and a different filter for detection of an emission wavelength. Typical values for bandpass are 10 to 50 nm. Filters can offer excellent out-of-bandpass rejection, but do not offer the flexibility of a spectrometer.
Cut-on and cut-off filters	absorb all radiation at wavelengths either shorter or longer than the transition wavelength. The cut-off wavelength is defined as the spectral position where 50 percent of the maximum trans- mission of the filter is observed
Neutral density (ND) filters	are virtually wavelength-independent in the 180 nm to 2.5μm spectral range. They transmit a specific percentage of the incident light; the exact trans- mission percentage can be very precise to allow strong signals to be measured on detectors that would otherwise be saturated. Use of ND filters enables greater dynamic range in a measurement system.

Other non-dispersive instruments such as interferometers are often used, especially in the infrared. They can have an advantage in terms of signal-to-noise compared with dispersive spectrometers, especially since in this region the radiation detectors are noisy. Fourier transform techniques are now the method of choice in this spectral region because the instruments have no entrance slits and, after collimation, the effective solid angle can be significantly larger than for a conventional spectrometer.

Dr. John R Gilchrist,
Gilden Photonics Ltd

References:

1. The Infrared Handbook, WL Wolfe & GJ Zissis, Office of Naval Research 1978
2. SpectroChemical Analysis, JD Ingle jr & SR Crouch, Prentice Hall 1988
3. The Design of Optical Spectrometer, JF James & RS Sternberb, Chapman & Hall Ltd., 1969
4. Spectrograph Design Fundamentals, John James, Cambridge Univeristy Press 2007
5. Diffraction Grating Handbook 6th Ed, C Palmer, The Grating Lab, Newport Corp 2005

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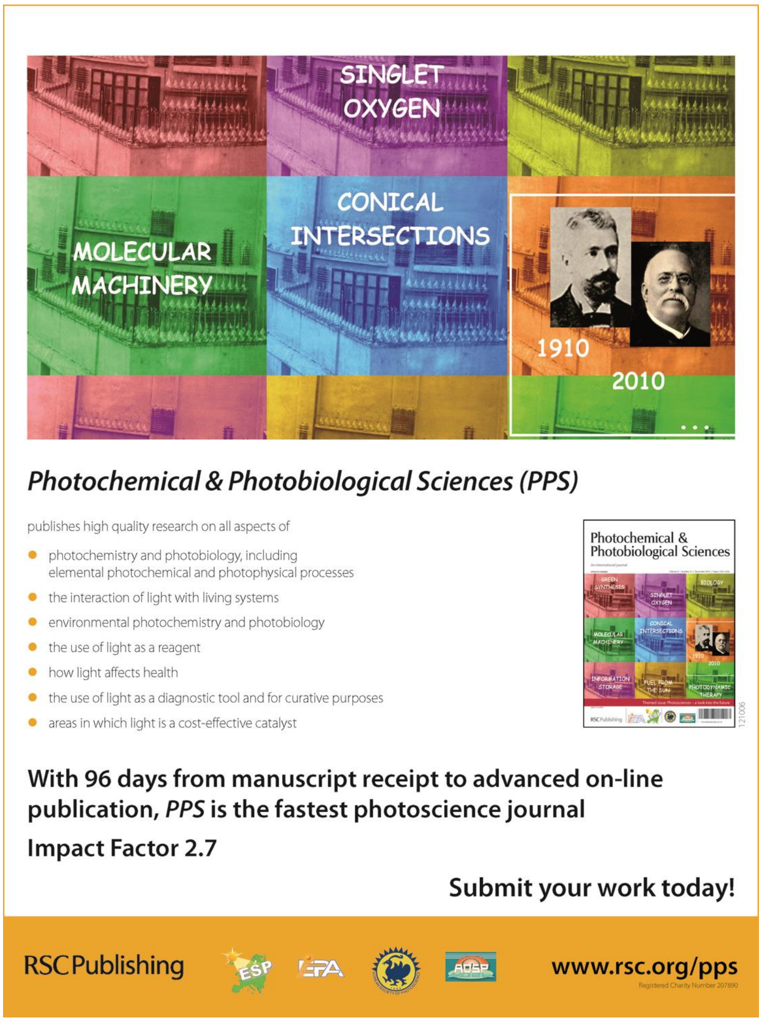

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The Exploration of Supramolecular Systems and Nanostructures by Photochemical Techniques

(P. Ceroni Ed., Springer, Lecture Notes in Chemistry, Vol. 78, Heidelberg, Germany, 2012)

This book is aimed at providing the newcomers of the field with an overview of the photophysical and photochemical techniques. It provides the basic concepts, without introducing too many technical and mathematical details, with the aid of self-explicative figures and schemes. The volumes presents the methodology to correctly perform a photochemical or photophysical experiment, as well as the most critical aspects of the laboratory application. It is of interest also to scientists already involved in the field because it offers technical and operative details useful in the laboratory, as well as references to current research, pioneering contributions, and review articles on specific aspects.

The essentials of a quantum mechanical treatment of the interaction of electromagnetic radiation with molecules is described in the first chapter, and the second one deals with supramolecular photochemistry, with particular emphasis on energy and electron transfer with a description of the Marcus theory. The following chapters are devoted to the different photochemical and photophysical techniques: spectrophotometry and spectrofluorimetry, actinometry, absorption and luminescence techniques with polarized light excitation, time-resolved absorption and luminescence spectroscopy, down to femtosecond resolution. Each chapter comprises both the theoretical basis and the practical aspects and describes an example of the application of these techniques to the study of a supramolecular system.

The editor, as well as the authors of the specific chapters, are well-known researchers in the field, and the result is a very useful book, which can be of interest to all researchers interested in

Supramolecular Photochemistry and, at the same time, is a valid entry to the newcomers, to which it is essentially directed. It could also be quite useful as a reference book for academic courses on Photochemistry.

Sebastiano Campagna
Università di Messina
Messina, Italy

Call for Nominations for the Grammaticakis-Neumann Award 2014 of the Swiss Chemical Society

The Grammaticakis-Neumann Prize of the Swiss Chemical Society is awarded to a promising young scientist for outstanding independent research in photochemistry, photophysics or molecular photobiology. At the time of the award the candidate may not be a tenured professor or a person in a higher position in industry, and should be younger than 40.
The prize is awarded annually and the prize sum is CHF 5,000.

Nomination

Nominations are invited from organizations and individuals. Self-nominations are admitted.
A nomination must include:

- A brief curriculum vitae (max 2 pages).
- A list of 5 of the nominee's most important scientific publications.
- A nomination letter.
- Not more than two seconding nomination letters.

The documents (language E/D/F) should be sent electronically as a single pdf file to info@scg.ch. Seconding letters should also be submitted electronically.
The deadline for all documents to reach the Swiss Chemical Society is September 30, 2013.

Past fife Grammaticakis-Neumann Prize Winners
2013: Dr. Uwe Pischel, Spain
2012: Prof. Hans Jakob Wörner, Switzerland
2011: Dr. Marina Kuimova, London
2010: Prof. Sivaguru Jayaraman, USA
2008: Prof. Alexander Heckel, Germany

More information on http://www.scg.ch/awards/

PORTER MEDAL

The Porter Medal 2014 – Call for Nominations

The Porter Medal is awarded every two years to the scientist who, in the opinion of the European Photochemistry Association, the Inter-American Photochemistry Society, and the Asian and Oceanian Photochemistry Association, has contributed most to the subject of Photochemistry. The Porter Medal, named for the late George Porter FRS, Nobel Laureate, is awarded biannually to the scientist who in the opinion of the judges, has contributed most to the science of photochemistry with particular emphasis on more physical aspects, reflecting George Porter's own interests.

To nominate European candidates for The Porter Medal 2014, candidate's details should preferably be sent directly to the President of the European Photochemistry Association, Professor Werner Nau (w.nau@jacobs-university.de). For nomination of candidates from other continents, see the Porter Medal webpage: http://www.portermedal.com. Nominations may also be sent to the Chair of the Porter Medal Committee, Professor David Klug. The nomination package should include:

- Curriculum Vitae of the candidate
- A list of publications
- A citation for the award, not exceeding five pages
- Two letters of reference

Provisional closing date for the receipt of nominations (based on the guidelines from previous years) will be 31 January 2014.

Previous winners:

1988	Lord Porter (George Porter), UK (Founding medal)
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1992	Kinichi Honda, Japan
1994	Nicholas J.Turro, USA

1995	J.C."Tito" Scaiano, Canada (Special Medal for London ICP)
1996	Noboru Mataga, Japan
1998	Frans de Schryver, Belgium
2000	Vincenzo Balzani, Italy
2002	Josef Michl, USA
2004	Graham R.Fleming, USA
2006	Howard E. Zimmerman, USA
	Hiroshi Masuhara, Japan
2008	Michael R. Wasielewski, USA
2010	David Philips, UK
2012	Thomas J. Meyer, USA

EPA Prize for Best PhD Thesis in Photochemistry
Call for Nominations

The EPA Prize for the best PhD thesis in photochemistry will be attributed during the XXVth IUPAC Symposium on Photochemistry which will be held in Bordeaux, France, in 2014. The awardee will present his/her work at the Symposium. The Prize is 1000 Euros, plus travel costs to Bordeaux (within the limit of 300 €) and one free year of EPA membership. The candidate must have defended his/her PhD thesis in 2012/2013 and be nominated by an EPA member. Nominations should be sent (electronically only) to Werner Nau (w.nau@jacobs-university.de). The nomination package should include:

- Curriculum Vitae of the candidate
- Copy of the thesis
- Abstract of thesis in English, no more than five pages
- List of publications arising from the thesis
- A letter of support.

Closing date for the receipt of nominations will be 31 December 2013.

Previous winners:

2008 Maria Abrahamsson (thesis supervisor: Leif Hammarström), Sweden, Alexandre Fürstenberg (thesis supervisior: Eric Vauthey), Switzerland

2010 Anne Kotiaho (thesis supervisior: Helge Lemmetyinen), Finland

2012 Karl Börjesson (thesis supervisior: Bo Albinsson), Sweden

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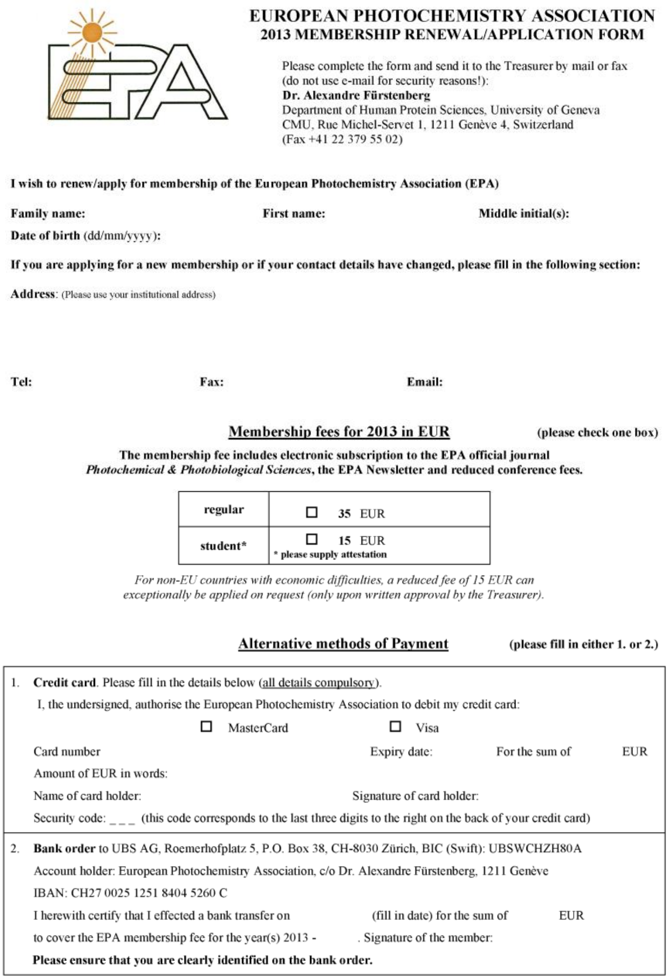

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