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No. 89, November 2015

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INTERNATIONAL
YEAR OF LIGHT
2015

EDITORIAL

President’s Letter

Dear Colleagues,

I’ll start in traditional fashion, by commenting on the weather! In the UK this is unseasonably mild, although the rain brought by storm Desmond has caused significant issues in many areas. Not usual climate behaviour for the UK, but of course drawing conclusions from one-off measurements is always hazardous – however there is long-term consensus (see below).

Paris has been the focus of two recent very significant events. The first coincided with the Royal Society of Chemistry awards evening in Manchester on 13th November, where many of those assembled, linked in to social media, saw with increasing dismay and horror events unfolding over the course of the evening . A minute of silent reflection was held before the Saturday morning meeting session. The second, and fortunately much more positive event was the historic agreement on climate change made over the past weekend, with a commitment to restrict global warming to below 2 degrees celcius. Clearly an ambitious target, and renewables including solar energy will play an important role – innovative solar energy conversion materials will be to the fore. Whether a hydrogen economy based on photocatalytic water splitting will dominate the world economy or whether battery technology coupled to renewable energy will win the day remains to be seen, but solar energy looks set to be an important part of the mix for the foreseeable future.

I was put in mind from these musings on energy generation of a discussion session held at the XIX IUPAC Symposium on Photochemistry in Budapest in 2002, where (if memory serves) the hypothesis was that “traditional” photochemistry was the past and that the future lay with supramolecular photochemistry and functional devices. One could argue this has largely come to pass, although issues surrounding for example photodegradation mechanisms – “traditional” photochemical kinetic analysis – remain. Perhaps a new debate at a future conference may be worth considering.

2016 will see the presenting of three awards in the area of photochemistry. These are the *EPA-PPS Prize* for the most highly cited paper published in PPS during the previous two calendar years, the *EPA Prize for Best PhD Thesis in Photochemistry* published during the previous two calendar years, and the *Porter Medal*, in cooperation with our Inter-American and Asian/Oceanian photochemistry association counterparts, I-APS and APA.

Finally, a reminder about our Facebook page; please "like" us to keep up-to-date with conferences, job opportunities and general news.

Dr. David Worrall
Loughborough University

PUBLICATIONS

The Photochemistry of the Future

Giacomo Ciamician

I think the best way to conclude the yar of light is to read the contribute that G. Ciamician published on Science. We have to thank the American Association for the Advancement of Science for the permission to publish here this article.

M.D'A.

Modern civilization is the daughter of coal for this offers to mankind the solar energy in its most concentrated form: that is in a form in which it has been accumulated in a long series of centuries. Modern man uses it with increasing eagerness and thoughtless prodigality for the conquest of the world and, like the mythical gold of the Rhine, coal is to-day the greatest source of energy ad wealth.

The earth still holds enormous quantities of it, but coal is not inexhaustible. The problem of the future begins to interest us and a proof of this may be seen in the fact that the subject was treated last year almost at the same time by Sir William Ramsay before the British Association for the Advancement of Science at Portsmouth and by Prof. Carl Engler before the Versammlung deutscher Naturforscher und Aerzte at Karlsruhe. According to the calculations of Prof. Engler Europe possesses today about 700 billion tons of coal and America about as much; to this must be added the coal of the unknown parts of Asia. The supply is enormous but, with increasing consumption, the mining of coal becomes more expensive on account of the greater depth to which it is necessary to go. It must therefore be remembered that in some regions the deposits of coal may become practically useless long before their exhaustion.

Is *fossil* solar energy the only one that may be used in modern life and civilization? That is the question.

Sir William Ramsay has made a very careful study of the problem from the English point of view. He has considered the various sources of energy such as the tides, the internal heat of the hearth, the heat of the sun, water power, the forests and even atomic disintegration, and has come to the conclusion that none can be practically used in England on account of her special contour and climate.

Though the internal energy of the earth may produce terrible disasters through volcanic eruptions and earthquakes, it can hardly be used by man. The energy derived from the rotation of the earth (tides) can hardly be counted upon on account of the enormous quantities of water that would have to be handled. Atomic disintegration has recently been treated in a brilliant lecture by Frederick Soddy, with special reference to the enormous energy changes which are involved. If man ever succeeds in availing himself of the internal energy of the atoms, his power will surpass by far the limits assigned to it today. At present he is limited to the use of solar energy. Let us see however whether the *actual* energy may not supplant that stored up in fossil fuel. Assuming that the solar constant is three small calories a minute per square centimeter, that is thirty large calories a minute per square meter or about 1800 large calories an hour. We may compare this quantity of heat with that produced by the complete combustion of a kilogram of coal, which is 8000 calories. Assuming for the tropics a day of only six hours sunshine we should have, for a day, an amount of heat equivalent to that furnished by 1.35 kg. of coal, or one kilogram in round numbers. For a square kilometer we should have a quantity of heat equivalent to that produced by the complete combustion of 1000 tons of coal. A surface of only 10,000 square kilometers receives in a year, calculating a day of only six hours, a quantity of heat that corresponds to that produced by the burning of 3650 million tons of coal, in round numbers three billion tons. The quantity of coal produced annually (1909) in the mines of Europe and America is calculated at about 925 million tons and, adding to this 175 million tons of lignite, we reach 1100 million tons or a little over one billion. Even making allowances for the absorption of heat on the part of the atmosphere and for other circumstances, we see that the solar energy that reaches a small tropical county – say of size of Latium – is equal annually to the energy produced by the entire amount of coal mined in the world! The desert of Sahara with its six million square kilometers received daily solar energy equivalent to six billion tons of coal!

This enormous quantity of energy that the earth receives from the sun, in comparison with which the part which has been stored up by the plants in the geological periods is almost negligible, is largely wasted. It is utilized in waterfalls (white coal) and by plants. Several times it utilization in a direct form through mirrors has been tried, and now some very promising experiments are being made in Egypt and in Peru; but this side of the problem is beyond my power to discuss and I do not propose to treat it here.

The energy produced by water power during the period of one year is equal to that produced by 70 billion tons of coal according to the data given in Professor Engler's lecture. It is however very small, as might be expected, in comparison with the total energy that the sun sends to earth every year. Let us now see what quantity of solar energy is stored by the plants: on the total surface of the various continents, which is 128 million square kilometers, there is a yearly production of 32 billion tons of vegetable matter, which, if burnt, would give the quantity of heat that corresponds to the total combustion of 18 billion tons of coal. It is not much but even this is 17 times as much as the total present production of coal and of lignite.

I

Now let us consider the first part of our subject. Is it possible or, rather, is it conceivable that this production of organic matter may be increased in general and intensified in special places, and that the cultivation of plants may be so regulated as to make them produce abundantly such substances as can become sources of energy or be otherwise useful to civilization? I believe that this is possible. It is not proposed to replace coal by organic substances produced by plants; but it is conceivable that this organic matter may be utilized more satisfactorily than is now the case.

It has frequently been said even by persons of authority that some day the transformation of coal into bread may become not only possible but economically desirable. According to these people that ideal of the future should be to produce through synthesis from coal all substances necessary for the alimentation of man: such substances as starch, sugar and fat, also proteins and perhaps cellulose; in other words to abolish agriculture altogether and to transform the world in to a garden of useless flowers. Never was a greater fallacy thought or expressed: the real problem is just the reverse of this. My friend Professor Angeli wisely called to my attention that, while the externals of life have been changed greatly by the progress of industry so as to use all our technical knowledge to increase our comfort, the quality and quantity of human alimentation have hardly changed at all; nay, a new science has come into existence (bromatology) to see that no artificial product of industry enters harmfully into our alimentation. At the time of Napoleon III an attempt was made to substitute gelatine for meat; but is was seen very soon – an now the reason for it is known by all – that this substitute could not be sufficient to maintain life. With the relatively small reserves of coal that the past geological epoch have stored for us, it will never be desirable to produce from coal what nature generously offers us through solar energy. It is on the other hand a work worthy of praise to attempt to make plants produce the fundamental substances in larger quantity. Modern agriculture tries to do this by intensive cultivation; but it is also desirable to make the plants store up solar energy and transform it into mechanical energy.

A well-known instance of this occurred when the development of the daily press in all civilized countries made it imperative to provide wood pulp in a sufficient quantity and at low prices. Trees, better adapted to the purpose, were soon found and they were those which, on account of their rapid growth, could furnish the necessary cellulose sooner. For the problem we are now considering the quality of the plants is of secondary importance; they may be herbs or trees; they may grow in swamps or dry places, on the sea coast or even in the sea; the essential point is that they grow fast or that their growth may be intensified. It would be like realizing the desire of Faust:

"Und Bäume die sich täglich neu begriüen!"

Mephistopheles did not consider a similar task impossible:

"Ein solcher Auftrag schreckt mich nicht,
Mit solchen Schätzen kann ich dienen"

Should we consider the task impossible, naturally in a more limited sphere, after so many centuries of culture? I do not believe so. The above estimate of the total production of organic matter over all the solid surface of the earth, that is of 32 billion tons a year, has for its basis the old calculation of Liebig of 2.5 tons per hectare. This may be considered even to-day the average production for all the earth. According to A. Mayer, through intensified culture the production may be increased to 10 tons per hectare and in tropical climates it may reach 15 tons. On a square kilometer it would be 1500 tons, corresponding to 840 tons of coal, while the solar energy received in a year by a square kilometer would be equivalent to about 300,000 tons of coal, the part of the total energy stored up by the plants being about 1/300. A great deal remains to be done, but if we consider that since Liebig, largely by adopting the methods proposed by him, the production has been a least quadrupled, we may hope to do much more in the future, especially if we are spurred on by necessity or even by convenience.

By increasing the concentration of carbon dioxide up to an optimum value (1 to 10% according to Kreusler) and by using catalyzers, it seems quite possible that the production of organic matter may be largely increased, making use, of course, of suitable mineral fertilizers and selecting localities adapted to the purpose owing to the climate or the condition of the soil. The harvest, dried by the sun, ought to be converted, in the most economical way, entirely into gaseous fuel, taking care during this operation to fix the ammonia (by the Mond process for instance) which should be returned to the soil as nitrogenous fertilizer together with all the mineral substances contained in the ashes. We should thus get a complete cycle for the inorganic fertilizing substances, the only waste being that common to all industrial processes. The gas so obtained should be burnt entirely on the spot in gas engines and the mechanical energy thus generated should be transmitted elsewhere or utilized in any way that seems advisable. We need not go into details. The carbon dioxide, resulting from the combustion, should not be wasted but should be returned to the fields. Thus the solar energy, obtained by rational methods of cultivation, might furnish low-priced mechanical energy, perhaps better than through the systems based on mirrors, because the plants would be the accumulators of the energy received by the earth.

But the problem of the utilization of plants in competition with coal has another and more interesting side. First of all we must remember the industries which have their basis in agriculture: the cotton and other textile industries, the starch industry, the production of alcohol and of all fats, the distillation of wood, the extraction of sugar, the production of tanning substances and other minor industries. All these industries are susceptible of improvement not only by the introduction of more advantageous technical devices in the treatment of the raw materials but also by a largely increased production of the raw materials. Let us think for an example of the progress made in the production of beet sugar.

The plants are unsurpassed masters of – or marvelous workshops for – photochemical synthesis of the fundamental substances, building up from carbon dioxide with the help of solar energy. They also produce the so-called secondary substances with the greatest ease. These latter are usually found in the plants in small quantity and are of value for special reasons. The alkaloids, glucosides, essences, camphor, rubber, coloring substances and others are of even greater interest to the public than the fundamental substances on account of their high commercial value. In this field a battle is raging between chemical industry and nature, a battle which does honor to human genius. Up to now the products prepared from coal tar have almost always been triumphant. I do not need to remind you the various victories; but it is possible that these may prove to have been Pyrrhic victories. A great authority on organic industries considered recently what would happen in case, for any reason, there were a rapid increase in the price of coal tar and consequently of the substances contained in it. He pointed out the inevitable effect of this on the coal tar industries. We all remember with admiration the story of the great difficulties that had to be met in the choice of the raw material for the production of indigo. It was necessary finally to use naphthalene because toluene could not be obtained in sufficient quantity. But it is not merely through a rise in the price of the raw materials that an industry may suffer; it may be brought to standstill by a diminished interest and activity in a certain field of scientific study. It has been thoroughly established that modern industry is affiliated very intimately with pure science; the progress of one determines necessarily that of the other. Now the chemistry of benzene and its derivatives does not constitute the favorite field of research as it did during the second half of the last century. The centre of interest is now to be found in the matters and problems connected with biology. Modern interest is concentrated on the study of the organic chemistry of organisms. This new direction in the field of pure science is bound to have its effect on the technical world and to mark out new paths for the industries to follow in the future.

It is a fact that lately several organic industries have been successfully developed, outside of the field of benzene and coal tar. There are flourishing industries in essences and perfumes and in some alkaloids, like coca. In these industries products, which plants produce in relatively large amounts, are converted into products of higher commercial value. For instance everybody knows that essence of violet is now made from citral contained in lemon oil. This is a line along which we ought to follow because we are certain of making progress. It is to be hoped that in the future we may obtain rubber commercially in some such way.

The question has still another side, which I believe deserves your attention; it concerns certain experiments recently made by myself together with Professor Ravenna at Bologna. It is not because we have arrived at any practical results that I refer to these experiments; but because they show definitely that we can modify to a certain extent the chemical processes that take place during the life of the plants. In a series of experiments made in an effort to determine the physiological function of the glucosides, we have succeeded in obtaining them from plants that usually do not produce them. We have been able, through suitable inoculations, to force maize to synthesize salicine. More recently, while studying the function of the alkaloids in the plants, we have succeeded in modifying the production of nicotine in the tobacco plant, so as to obtain a large increase or a decrease in the quantity of this alkaloid. This is only a beginning, but does it not seem to you that, with well-adapted systems of cultivation and timely intervention, we may succeed in causing plants to produce, in quantities much larger than the normal ones, the substances which are useful to our modern life and which we now obtain with great difficulty and low yield from coal tar? There is no longer at all of using for industrial purposes land which should be devoted to raising foodstuffs. An approximate calculation shows that on the earth there is plenty of land for both purposes, especially when the various cultivations are properly intensified and rationally adapted to the conditions of the soil and the climate. This development is a real problem of the future.

II

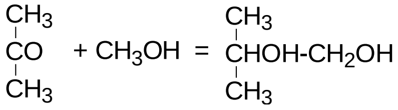
Technical organic industry may yet expect great help from photochemistry understood in the sense above expressed and in the competition between this and the chemistry of coal tar will be a great incentive for new progress. It is also true that human genius will always tend to proceed along lines selected by itself, and there is no question but that the great development in the coal tar industry has been due in part to this splendid spirit of independence. It may be asked whether there are not other methods of production which may rival the photochemical processes of the plants. The answer will be given by the future development of photochemistry as applied to the industries and on this I have a few ideas to express. The photochemical processes have not had so far any extensive practical application outside of the field of photography. From its very beginning photography has aroused a great deal of interest: it was taken up technically and, as usually happens in similar cases, it had a rapid and brilliant success. But notwithstanding the many applications photography represents only a small part of photochemistry. So far, photochemistry has only been developed to a very slight extent, perhaps because chemists have been attracted by problems which seemed more urgent. So it happens that while thermochemistry and electrochemistry have already reached a high degree of development, photochemistry is still in its infancy. Now, however, we notice a certain awakening due to a series of studies concerning general problems and special processes, especially in the organic field, in which my friend Dr. Paul Silber and myself have taken an active part. Two recent publications, one of Plotnikow and the other by Benrath bear witness to this. But much remain to be done both in theoretical and general photochemistry as well as in the special branches. The photochemical reactions follow the fundamental laws of affinity, but have a special character. They are especially notable for the small temperature coefficient and are, however, comparable – a fact which is not without technical importance – to the reactions which take place at very high temperatures. According to a brilliant idea of Plotnikov, luminous radiations produce a different ionization from that due to electrolytic dissociation; the separation of an ion requires a quantity of light which is determined by the theory of Planck and Einstein. The question is therefore related to the most recent and profound speculations of mathematical physics.

For our purposes the fundamental problem from the technical point of view is how to fix the solar energy through suitable photochemical reactions. To do this it would be sufficient to be able to imitate the assimilating processes of plants. As is well known, plants transform the carbon dioxide of the atmosphere into starch, setting free oxygen. They reverse the ordinary process of combustion. It has always seemed probable that formaldehyde was the first product of the assimilation; and Curtius has at last demonstrated its presence in the leaves of the beech trees. The artificial reproduction of a similar process by means of ultraviolet rays has already been obtained by D. Berthelot. With convenient modifications could not this now actually be done on the tropical highlands? Yet the true solution consists in utilizing the radiations that pass through the entire atmosphere and reach the surface of the earth in large amounts. That a way of accomplishing this exists is proved by the plants themselves. By using suitable catalyzers, it should be possible to transform the mixture of water and carbon dioxide into oxygen and methane, or to cause other endo-energetic processes. The desert regions of the tropics, where the conditions of the soil and of the climate make it impossible to grow any ordinary crops would be made to utilize the solar energy which they receive in so large a measure all the year, that the energy derived from them would be equal to that of billions of tons of coal.

Besides this process, which would give new value to the waste products of combustion, several others are known, which are caused by ultraviolet radiations and which might eventually take place under the influence of ordinary radiations, provided suitable sensitizers were discovered. The synthesis of ozone, of sulphur trioxide, of ammonia, of the oxides of nitrogen, as well as many other syntheses, might become the object of industrial photochemical processes.

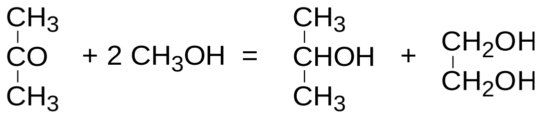
It is conceivable that we might make photoelectrical batteries or batteries based on photochemical processes, as, for instance, in the experiments of C. Winther.

Passing to the field of organic chemistry, the reactions caused by light are so many that it should not be difficult to find some which are of practical value. The action of light is especially favorable to processes of reciprocal oxidation and reduction which give rise to or are associated with phenomena of condensation. Since the common condensation is that of the aldolic type there is much hope for the future, the aldolic condensation being the fundamental reaction of organic synthesis. Some experiments recently made by my friend Silber and by myself may serve here as an illustration. The simplest case is that of the action of light on a mixture of acetone and methyl alcohol in which



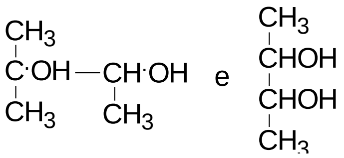
$$\begin{matrix}CH_3\\ |\\ CO\\ |\\ CH_3\end{matrix} + CH_3OH = \begin{matrix}CH_3\\ |\\ CHOH\text{-}CH_2OH\\ |\\ CH_3\end{matrix}$$

Isobutylene glycol is produced. But this condensation which may be considered as a simultaneous process of oxidation and reduction, is accompanied by the reduction of the ketone to isopropyl alcohol and by the oxidation of the methyl alcohol to formaldehyde, which latter however, does not remain as a product which can be isolated because it reacts with the remaining methyl alcohol and is transformed into ethylene glycol:



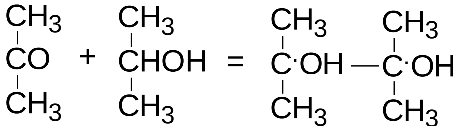
$$\begin{array}{c}CH_3\\|\\CO\\|\\CH_3\end{array} + 2\,CH_3OH = \begin{array}{c}CH_3\\|\\CHOH\\|\\CH_3\end{array} + \begin{array}{c}CH_2OH\\|\\CH_2OH\end{array}$$

Applying the same photochemical reaction to the mixture of acetone and ethyl alcohol we have analogous products: trimethylene glycol and along with this isopropyl alcohol and dimethylethylene glycol:



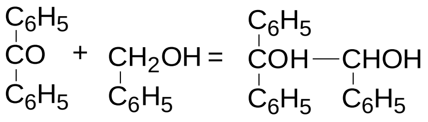
$$\begin{array}{ll}CH_3 & \\ | & \\ C\cdot OH - & CH\cdot OH\\ | & |\\ CH_3 & CH_3\end{array} \quad e \quad \begin{array}{c}CH_3\\|\\CHOH\\|\\CHOH\\|\\CH_3\end{array}$$

With acetone and isopropyl alcohol, as could be expected, there is formed only pinecone:



$$\begin{array}{c}CH_3\\|\\CO\\|\\CH_3\end{array} + \begin{array}{c}CH_3\\|\\CHOH\\|\\CH_3\end{array} = \begin{array}{ll}CH_3 & CH_3\\ | & |\\ C\cdot OH - & C\cdot OH\\ | & |\\ CH_3 & CH_3\end{array}$$

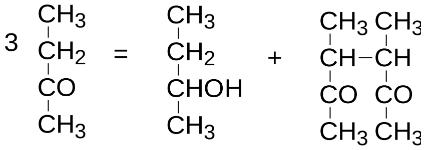
In the aromatic series benzophenone and benzyl alcohol give triphenylethylene glycol, together with other products:



$$\begin{array}{c}C_6H_5\\|\\CO\\|\\C_6H_5\end{array} + \begin{array}{c}CH_2OH\\|\\C_6H_5\end{array} = \begin{array}{ll}C_6H_5 & \\ | & \\ COH - & CHOH\\ | & |\\ C_6H_5 & C_6H_5\end{array}$$

This was the first case in which this condensation has been observed; others were afterwards studied by Paternò, who replaced the benzyl alcohol by several other aromatic substances. The observations of Klinger showed that the aldehydes also underwent condensations ant this has since been confirmed by Benrath.

To get an idea of the variety of photochemical reactions we may confine ourselves to a systematic study of the ketones and alcohols. In ordinary organic chemistry the reactions often take place in some definite way; but the photochemical reactions often furnish surprises and proceed along quite different lines. From the very first experiments we knew that benzophenone did not form addition products with ethyl alcohol, but was converted into pinecone at the expense of the alcohol, which was oxidized to aldehyde. Proceeding with the study of aliphatic ketones, similar to acetone, we have this year discovered a remarkable fact. Methylethylketone condenses with itself and forms the paradiketone, reducing itself at the same time to secondary butyl alcohol:

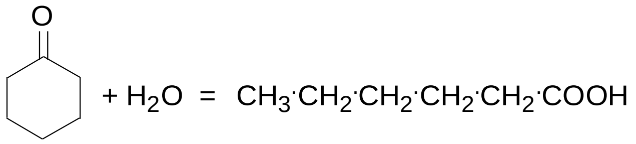


$$3\,CH_3-CH_2-CO-CH_3 = CH_3-CH_2-CHOH-CH_3 + CH_3-CO-CH(CH_3)-CH(CH_3)-CO-CH_3$$

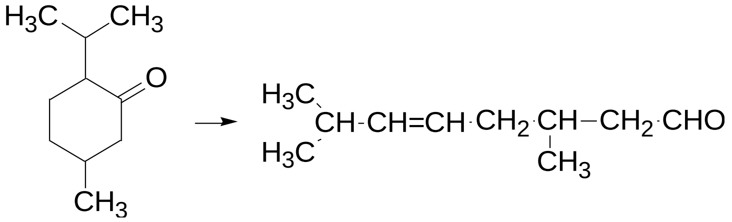
Of course the synthesis of diketones by light could not an isolated reaction; we had previoulsly noticed the formation of diacetyl: acetonylacetone is found, as we now know, among the products of acetone in solution in ethyl alcohol and it is also possible that the metadiketones, such as acetylacetone for instance, may be prepared photochemically. These reactions have a special importance on account of the special character of the diketones and their tendency to change in all sorts of ways. From them derivatives of benzene can be obtained as well as of pyrrazol and isoxazol, of quinoline, of furfurol, of thiophene and of pyrrol. In regard to this last change I wish to remind you that tetramethylpyrrol corresponds to the paradiketone previously referred to. If I dare to be reckless, as you may see I am at this moment, contrary to my custom, but perhaps urged thereto unconsciously by the American genius which heeds no obstacles, I may refer to the relations between the polysubstituted pyrrols with alcohol radicals and chlorophyll, and I may see in these reactions the possibility of the synthesis of this fundamental substance by means of an artificial photochemical process. Its formation in plants, like its function, is due to a photochemical process; we do not know, however, whether and in what measure light enters into all the synthetic plant reactions, from which originate the various substances which we find in plants. The research should proceed together in two fields; phytochemistry and photochemistry will be of great help one to another. Industrially this co-operation might have a great future: the raw materials obtained from the plants might be refined through artificial photochemical processes.

Lately we have been interested intensely by the changes that some substances of the group of the terpenes and of the camphors undergo when exposed to light, especially through hydrolytic processes. So far, indeed, our experiments have taught us that light can spoil rather than improve essences.

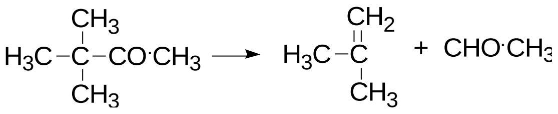
The cycloketones, for instance, are hydrolyzed and give the corresponding fatty acids; the cycloesanone gives capronic acid and menthone gives decylic acid.



In photochemistry, however, one reaction does not exclude the other; the reactions may be reversed as some recent experiments with ultraviolet rays demonstrate; for the ultraviolet rays sometimes reverse reactions caused by less refrangible radiations. It is important to find suitable sensitizers and catalyzers. We can see what the future has in store for us from such reactions as the photolysis of the ketones, which often accompanies the hydrolysis, and by means of which we prepare isocitronellal, for instance from menthone,



or the transformation of camphor into an unsaturated cycloketone, etc. The analogous breaking down of pinacoline into butylenes and acetic aldehyde



$$\mathrm{H_3C{-}\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}{-}CO{\cdot}CH_3 \longrightarrow H_3C{-}\overset{\overset{CH_2}{\|}}{\underset{\underset{CH_3}{|}}{C}} + CHO{\cdot}CH_3}$$

Is remarkable because it demonstrates what violent decompositions light may cause. It may be an enemy, but just on account of that it is necessary to be familiar with the weapons of the adversaries in order to be able to conquer them and avail ourselves of their strength.

I do not believe, however, that the industries should wait any longer before taking advantage of the chemical effects produced by light. The polymerizations, the isomeric changes, the reductions and oxidations with organic and inorganic substances, and the autoxidations which light causes so easily should already find profitable applications in some industries if researches were carried out carefully with this in mind. The action of light on nitric and nitrosilicic compounds, as we know it from experience, is one that ought to be utilized profitably. Our own transformation of orthonitrobenzoic aldehyde into nitrosobenzoic acid has recently been studied by various chemists, and has been made use of by Pfeiffer, who prepared a nitrophenylisatogen from chlorodinitrostilbene. This reminds us of the not less known transformation of benzylidene orthonitroacetophenone into indigo by Engler and Dorant and makes us foresee a new field in the photochemical production of artificial colors and dye-stuffs. The scope of studies on this subject ought not to be limited to preserving colors from fading, bleaching and all changes produced by light. The photochemistry of colors and dye-stuffs ought to furnish new methods of preparation and of dyeing. Very encouraging xperiments have already been made with diazoic compounds and mention should be made of the recent observation of Baudisch that α-nitrosonaphthylhydroxylamine is changed on the fibre to azoxynaphthalene when exposed to light. The autoxidation of leuco compounds by light is an old practice of which the ancients availed themselves for preparing purple; now the process is explained, thanks to the familiar researches of Friedlander, but it is clear that a great deal remains to be learned in this field.

Phototropic substance, which often assume very intense colors in the light, and afterwards return in the darkness to their primitive color, might be use very effectively. Such substances might well attract the attention of fashion rather than fluorescent materials which give the impression of changing colors. The dress of a lady, so prepared, would change its color according to the intensity of light. Passing from darkness to light the colors would brighten up, thus conforming automatically to the environment: the last word of fashion for the future.

Solar energy is not evenly distributed over the surface of the earth; there are privileged regions, and others that are less favored by the climate. The former ones would be the prosperous ones if we should become able to utilize the energy of the sun in the way which I have described. The tropical countries would thus be conquered by civilization which would in this manner return to its birth-place. Even now the strongest nations rival each other in the conquest of the lands of the sun, as though unconsciously foreseeing the future.

Where vegetation is rich, photochemistry may be left to the plants and by rational cultivation, as I have already explained, solar radiation may be used for industrial purposes. In the desert regions, unadapted to any kind of cultivation, photochemistry will artificially put their solar energy to practical uses.

On the arid lands there will spring up industrial colonies without smoke and without smokestacks; forests of glass tubes will extend over the plains and glass buildings will rise everywhere; inside of these will take place the photochemical processes that hitherto have been the guarded secret of the plants, but that will have been mastered by human industry which will know how to make them bear even more abundant fruit than nature, for nature is not in a hurry and mankind is. And if in distant future the supply of coal becomes completely exhausted, civilization will not be checked by that, for life and civilization will continue as long as the sun shines! In our black and nervous civilization, based on coal, shall be followed by a quieter civilization based on the utilization of solar energy, that will not be harmful to progress and to human happiness.

The photochemistry of the future should not however be postponed to such distant times; I believe that industry will do well in using from this very day all the energies that nature puts at its disposal. So far, human civilization has made use almost exclusively of fossil solar energy. Would it not be advantageous to make better use of radiant energy?

Interstellar photochemistry was shown to provide icy building blocks of life

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Where did the molecular ingredients for life on Earth come from? Many scientists think the basic chemical building blocks for biology were delivered via comets, but the building blocks – and the building process – remain a mystery.

In 2015 an international team led by Prof. Dr. Meierhenrich at the University Nice Sophia Antipolis has found lab-based evidence that a class of complex organic molecules evolved by photochemical reactions in the ice of star-forming clouds – and could be a potential source for the organic matter that allowed life on Earth to emerge. The findings, published in the *Proceedings of the National Academy of Sciences* 112, **2015**, 965–970, could also offer a chemical tip sheet for the European Space Agency's comet-chasing Rosetta mission, giving it hints as to which chemicals to look for.

The team was interested in what are called "evolved interstellar ices." These ices hang out in dense molecular clouds that give birth to a star and its surrounding solar system. As the star forms and the planets and comets and asteroids coalesce out of this debris, these ices are incorporated within them. The ices contain many familiar molecules: water, carbon monoxide, carbon dioxide, methanol, ammonia and methane – some of which are found on Earth in biological contexts. Comets or asteroids packed full of these ices could have delivered life-giving molecules to Earth, the thinking goes.

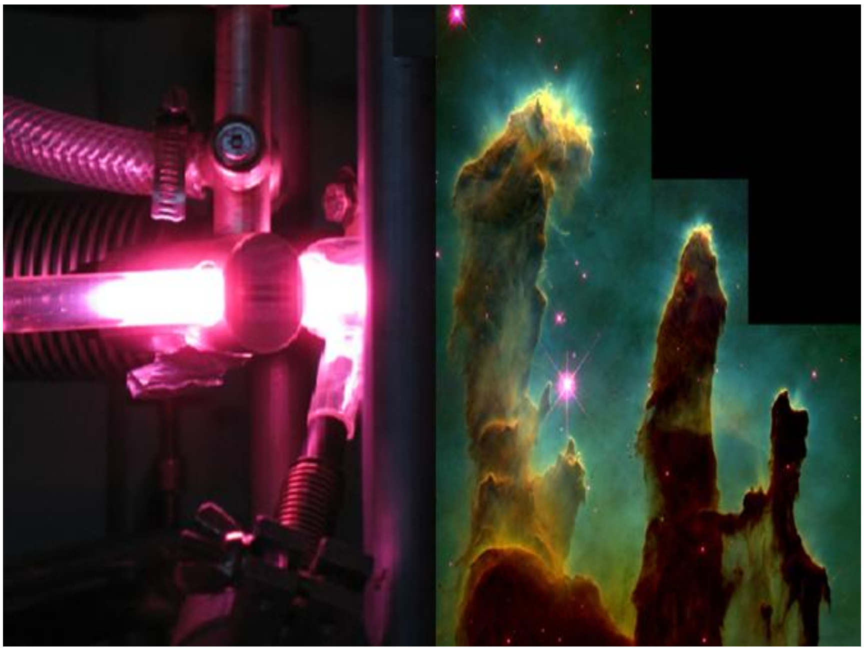

***Figure** : Ultraviolet processing of interstellar ice analogues (left) may represent a template of the natural evolution of interstellar ices observed in molecular clouds (right) and leading to the simultaneous formation of amino acids and sugars (de Marcellus et al., Proceedings of the National Academy of Sciences 112, **2015**, 965–970)*

However, it takes a lot of photochemistry to get from simple molecules to the complex strings that make up a macromolecule such as RNA (which is what scientists think coded the genetic instructions for living things before the emergence of DNA). How and where did all that chemistry happen? As it turns out, a lot of photochemistry is happening in the supposedly dead emptiness of space. It may not sound as conducive to cooking up complex organic molecules as the bubbling "primordial soup" we picture on early Earth, but space can be a chemically dynamic place, too. Ultraviolet radiation can produce radicals in the ice that recombine into ever-more-intricate molecules over time.

So, the photochemistry happening in this space ice could be doing a lot of grunt work before these molecules ever reach a planet, producing the kinds of complex organic compounds that would be essential for life to emerge. And since stars in general form out of these ice-filled molecular clouds, it could be happening all over the place. It could be the same way that organic molecules are delivered to life-friendly exoplanets, too. Possibly at the origin of the organic matter in our solar system and incorporated into planetesimals, this material may be considered as a potential source for prebiotic chemistry on rocky planets, following a process that may be quite universal. The problem is, it's not easy to study the evolution of these ices in the vastness of outer space. So the scientists set up an experiment in the laboratory where they could simulate the conditions of outer space, and watch what compounds were made when they subjected the basic starting materials (i.e. water, methanol, ammonia) to the harsh interstellar photochemical processes.

Previous photochemical work of the Meierhenrich team published in *Nature* 416, **2002**, 403–406 had turned up many intriguing organic compounds, including amino acids – essential molecules that today serve as the building block of proteins. But in this new experiment, the scientists actually found a whole other class of compound called aldehydes – 10 of them, including two sugar-related molecules called glycolaldehyde and glyceraldehyde. These two sugar-related compounds are considered as key prebiotic intermediates in the first steps toward the synthesis of ribonucleotides in a planetary environment. So this lab-based experiment reveals that these interstellar ices could hold the potential starting materials for RNA – and thus, so could any comet or asteroid that coalesced out of these ices (provided they haven't been altered beyond recognition in the intervening billions of years).

Evidence in the lab is one thing. The next step would be to actually identify these compounds in their natural setting, perhaps by using the new Atacama Large Millimeter Array telescopes to look for glyceraldehyde. Both compounds could be searched for in comets as well in certain carbonaceous chondrite meteorites. The findings also provided useful guidance for the Rosetta mission, whose Philae lander touched town on Comet 67P/Churyumov-Gerasimenko on November 12th, 2014 and woke up in June 2015. Philae's Cometary

Sampling and Composition (COSAC) instrument has a device that's designed to look for such organic molecules. A first set of organic molecules identified by COSAC after landing on the cometary nucleus will be published in July 2015 in Science (Goesmann, Meierhenrich et al. *Science*, **2015**, manuscript accepted for publication).

PORTER MEDAL

The Porter Medal 2016 – 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 2016, candidate's details should preferably be sent directly to the President of the European Photochemistry Association, Professor David Worrall (d.r.worrall@lboro.ac.uk). 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 2016.

Previous winners:

1988	Lord Porter (George Porter), UK (Founding medal)
1990	Michael Kasha, USA

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
2014	Masahiro Irie, Japan

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 CECP 2016 Meeting which will be held in Bad Hofgastein, Austria, in 2016. The awardee will present his/her work at the Symposium. The Prize is 1000 Euros, plus travel costs to Bad Hofgastein (within the limit of 300 €) and one free year of EPA membership. The candidate must have defended his/her PhD thesis in 2014/2015 and be nominated by an EPA member. Nominations should be sent (electronically only) to David Worrall (d.r.worrall@lboro.ac.uk). 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 2015.

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
2014	Giuseppina La Ganga (thesis supervisor: Sebastiano Campagna), Italy

SPECIAL REPORTS ON "THE YEAR OF LIGHT"

Introduction

Dear EPA members,
This year is a special one in our field of research. The EPA Newsletter is a good vehicle for reporting all the efforts made by experts in this area related to the "International Year of Light". The International Year of Light aims to communicate to society, at different levels of knowledge, the relevance of light in our lives, its presence in current and future technologies, and its potential for environmental remediation, among other advantages. The December 2015 issue is dedicated to collecting information about the events/activities of the "International Year of Light".
Researchers from different countries have provided information and/or webpage links reporting on activities performed in their country and all over the world as well as a general history of light and a discussion on future research challenges in this area. In this issue, *Silvia Braslavsky* informs and gives webpage links of a large number of activities that have been carried out in different countries on the occasion of the IYL or activities that will be celebrated in December or the beginning of 2016. *Michael Oelgemöller* provides information on a special issue of the *Australian Journal of Chemistry* with contributions by relevant photochemistry researchers and reports on exhibitions on ongoing research activities in photochemistry and photophysics in Australia. In addition, *Michael Oelgemöller* and *Karine Loubiere* reports on a special issue of the journal *Chemical Engineering & Tecnology* in recognition of the IYL and light-based technologies. *Michael Tausch* and *Axel Griesbeck* reflect on how to introduce basic photochemistry/photophysics at school and at university so that many occurrences in our lives, as well as technological developments, do not go unnoticed whatever the student's level of scientific knowledge. Information on activities carried out by researchers from the German Chemical Society involved in photochemistry in basic and applied research is also given. In addition, activities focused on teaching photophysics/photochemistry at all levels with valuable and attractive experiments are discussed. *Guillermo Orellana* informs on a hands-on workshop for 11th grade high school students in Madrid

and *Maria Gonzalez Béjar* reports on a workshop for graduate and undergraduate students at the University of Valencia and other activities in the Valencian region. *Malcolm D. E. Forbes* provides a general history of light and its applications, as well as future research challenges in many research areas in which light is the origin of the subsequent processes.
The EPA committee is very grateful to all of you who have collaborated in this issue.

Julia Pérez-Prieto
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The International Year of Light and Light-based Technologies (IYL)

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This is a very partial report of several activities related to the International Year of Light (IYL) designated by the United Nations and UNESCO (http://www.light2015.org/Home.html).

► A prominent activity initiated by photochemists was the creation of the web page by Axel Griesbeck (presently Secretary of the Organic and Bioorganic Chemistry Division of IUPAC) and Michael W. Tausch in the site of the University of Wuppertal: http://www.iyl2015.uni-wuppertal.de/. Although this page is mostly in German focusing on its use by the German teaching and student communities, there are several parts in English and is a very entertaining and multitask web site, which has the support of the Specialized group on Photochemistry within the German Chemical Society. Several easy-to-perform experiments with and about light are described. In this page there is also a **list of events** celebrating the IYL in many Countries, including the "27th International Conference on Photochemistry" in Jeju Island, Korea, from June 28th to July 3rd, 2015.

► The Inauguration of the IYL took place in Paris, at the UNESCO Building on 19th -20th January 2015. I was invited by the Argentinian Physical Society to participate in the event, as a member of the Argentinian delegation (see photo below). Many activities, as well as the calendar of activities in many Countries can be found at: http://www.light2015.org/Home.html

Figure 1: From left: Eli Sirlin, an Argentinian Light Architect, Beatriz García, an Argentinian Astronomer and Silvia Braslavsky, before the replica of the "Camera Obscura", as built by Alhazen 1000 years ago, and a statue of Alhazen.

► 2015 marks the 1000 years of the appearance of the 7-volumes treatise on Optics by Ibn al-Haytham, known in the West world as Alhazen, and his discovery of essential optical laws, such as the inversion of an image when the light reflected by the object passes through a pin-hole. His discoveries were honoured in Paris, among other things, with an extensive exhibition on the role played by Arab researchers in optics and related matters 1000 years ago. Extensive information is found at http://www.light2015.org/Home/ScienceStories/1000-Years-of-Arabic-Optics.html. The exhibition was prepared by the British association called 1001 Inventions (https://en.wikipedia.org/wiki/1001_Inventions).

► The "History of Light" and the discussions about its nature were also depicted in the exhibition. There is a beautiful video in youtube about this matter: https://www.youtube.com/watch?v=OLCqaWaV6jA

► Several initiatives related to the "Use of Light-based Technologies for Development", stressing the use of LED's and other affordable technologies were presented during the opening ceremony (http://www.light2015.org/Home/LightForDevelopment.html). Most of them extended during the year and beyond.

► 2015 marks also the Centenary of the Relativity Theory as enunciated by Einstein in 1915 and this was remarked several times during the 5 talks offered by Nobel Laureates during the opening ceremonies. They were: Ahmed Zewail (USA, Chemistry 1999), Steven Chu (USA, Physics, 1997), Zhores Alferov (URSS, Physics, 2000), William Phillips (USA, Physics, 1997), and Serge Haroche (France, Physics, 2012). The very entertaining talk by William Phillips can be found at:
https://www.youtube.com/watch?v=DmBmegutsds

► The question of the "Controlled use of Artificial Light" in order to be able to receive and monitor the Universe light (Cosmic rays) was posed by the Astronomers, i.e., "Dark-skies-Awareness" and "Avoidance of Light Pollution". Several practical measures were suggested to be adopted to meet these goals:
http://www.light2015.org/Home/CosmicLight/Dark-Skies Awareness.html. A price-affordable telescope (Galileoscope, http://www.optcorp.com/telescopes/refractor-telescopes/galileoscope-telescope- kit.html) was presented during the exhibition at the inauguration ceremony.

► "Light and Art and Culture" was another question handled during the opening ceremony and beyond: http://www.light2015.org/Home/LearnAboutLight/Art-and-Culture.html. All forms of art and art-restoration with light-based technologies as well as light and architecture were discussed. There was an impressive exhibition of nature pictures and some holograms.

►"Light in Life" was another subject:
http://www.light2015.org/Home/LearnAboutLight/Light-in-Life.html. The health related uses of light and the dangers of over-exposure to UV light, as well as the role of light in the sustainment of life (photosynthesis) and detection (vision) were the subject of presentations.

► An interesting discussion about "Scientific Policies" related to light and light-based technologies was held at the end of the two-days ceremonies with the participation of scientists from Africa, Latin America, Europe and the USA.

► I would like to mention the web page of the IYL as celebrated in Argentina: http://2015luz.com.ar/. Meetings, conferences, shows and exhibits about various aspects of the use of light have taken place. Activities for school-age children were presented in the whole Country as well as film exhibitions. The opening event in Argentina was an open-skies laser-light show in January 2015 in Mar del Plata (a beach resort in the Province of Buenos Aires).

►The 2nd Graduate school called "Optoandina" takes place in Quito (Ecuador) from November 8th to 12th for PhD students (mostly physicists) from Latin America: http://optoandina.wix.com/optoandina2. Within its frame I will be giving some lectures with general concepts of Photochemistry and Photobiology. The IYL is celebrated during the event.

A very large number of activities on the ocassion of the International Year of Light and Light-based Technologies (IYL) have taken and are taking place in many Countries. These activities have surely contributed to create a deeper perception among the population about the controlled use of natural resources and the possibilities of new technologies as well as about general concepts in physical and natural sciences. A calender for each Country can be found by clicking the selected Country at http://www.light2015.org/Home/About/Country.html

It has been and still is an enlightning year.

The International Year of Light and Light-based Technologies 2015 in Down Under

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https://research.jcu.edu.au/portfolio/michael.oelgemoeller/

Special Issue of the Australian Journal of Chemistry – In celebration of the '**International Year of Light and Light-based Technologies (IYL 2015)'** the *Australian Journal of Chemistry* published a dedicated special issue in November 2015.[1] The cover featured the IYL 2015 logo on top of a picture of Sauders Beach in North Queensland (Figure 1).

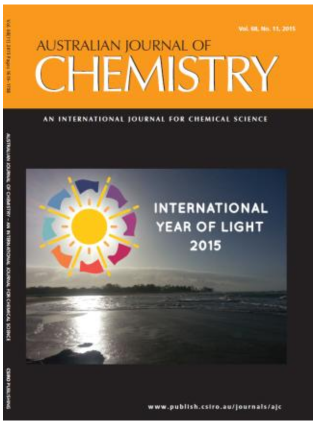

Figure 1. Front cover of the special issue.

Associate-Professor Michael Oelgemöller and Dr George Vamvounis from James Cook University (JCU) served as guest-editors. The special issue comprises 22 research articles that highlight recent achievements in photochemistry, spectroscopy and photophysics from across the world.

Norbert Hoffmann reviews TiO_2 photocatalysis in organic synthesis, whereas Eietsu Hasegawa and Shin-ya Takizawa summarize applications of 2-aryl-1,3-dimethylbenzimidazolines in photoinduced electron-transfer reactions. In a follow-up research paper, Hasegawa and his group describe metal-free reductions of organohalides promoted by visible light using these materials. Solar brominations under continuous-flow conditions are reported by Chan Pil Park et al, while Shinichiro Fuse and co-workers realize the multistep Arndt-Eistert synthesis in a microreactor. Oelgemöller and his group describe photodecarboxylative benzylations, which are subsequently transferred to an advanced continuous-flow photoreactor system. Yasuharu Yoshimi et al generate carbanions through photodecarboxylations and trap these with benzaldehyde. Intramolecular cycloadditions are used by Andrei Kutateladze and his team for the construction of unusual molecular architectures, whereas Thorsten Bach and co-workers realize enantioselective rearrangements catalyzed by a chiral bifunctional xanthone. Tadashi Mori et al investigate diastereoselectivities of the釘Paternó-Büchi reaction of chiral cyanobenzoates. Abe and co-workers describe triplet and singlet cyclopentane-1,3-diyl diradicals generated photochemically, while Anna Gudmundsdottir and her team report on a non-conjugated triplet 1,2-biradical. Rosalie Hocking and colleagues study sodium birnessite-based films to improve solar fuel technology, whereas George Vamvounis et al utilize photochromic compounds as sensors for explosives detection. Florian Baur and Thomas Jüstel describe the phosphorescence efficiency of lanthanide-based red phosphors materials, whereas Ulrich Kynast and co-workers study solid-state luminescence of rare earth diclofenac complexes. Yuning Li and his team investigate charge transport in a diketopyrrolopyrrole-based polymer, while Tim Bender et al describe new light-absorbing aryl-substituted boron subphthalocyanines. Seth Rasmussen and co-workers report on light-absorbing thieno[3,4-b]pyrazine-flourene copolymers, whereas David Lewis et al study fullerene content in polymers. The group of Kenneth Ghiggino describe a novel light absorbing copolymer based on benzodithiophene and [3,4-c]pyrrole-4,6-dione. Lastly, Hongxia Wang and colleagues report on perovskite solar cells based on nanocrystalline SnO_2.

The content of this special issue clearly reflects the multidisciplinary nature and importance of ‘light’ in the chemical and physical sciences.

Other contributions and activities – This year’s internet portal ‘Aktuelle Wochenschau (Current Weekly News)’ of the German

Chemical Society (GDCh) is dedicated to the International Year of Light.[2] The portal publishes weekly outreach articles that highlight the importance of light in science and medicine to the public. Associate-Professor Michael Oelgemöller from JCU contributed two articles. The advantages of photochemical synthesis under flow conditions over batch processes are highlighted in Week 42. In the subsequent contribution in week 43, the same author summarizes the achievements of solar chemistry from the historic beginnings of photochemistry to modern solar manufacturing of fine chemicals. The importance of solar (photo)chemistry for the prevention, treatment and cure of insect-borne diseases is likewise highlighted in an earlier submission to the *EPA Newletters*.[3]

At the University of Melbourne in Victoria IYL 2015 was celebrated with an exhibition of lamps, spectroscopic instrumentation, and materials from the School of Chemistry's Cultural Collection that dates from the 1850's. The exhibit items were complemented with drawings by artist Peter Sharp. The Exhibition "*Illuminated: through the prism of chemistry*" was opened with a lecture by Dr Renee Beale, Curator of the collection, and Peter Sharp including a display of artwork projections on the exterior of the Chemistry Building.[4]

Likewise, photochemical and solar reactors were showcased at JCU's open day in Townsville in November (Figure 2). This exhibition was complemented by posters on ongoing photochemical research at JCU.

Figure 2. Chemistry stand at JCU's open day 2015 (with research posters in the background) and some of the photochemical gear shown.

Overall, the IYL 2015 has seen several activities in Down Under. These nicely represent the ongoing research activities in photochemistry, spectroscopy and photophysics within the Australasian region.[5]

Acknowledgment – MO thanks emeritus Professor Curt Wentrup (editor-in-chief) of the Australian Journal of Chemistry for supporting the special issue.

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International Year of Light 2015 Report on GDCh Activities

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More Light!

„More Chemistry with Light! More Light in Chemistry!“ Under this title the editorial of the Special Issue of the GDCh-journal Angew. Chem. Int. Ed. (2015, 54, 11294-11295, see cover reproduced with permission of Wiley-VCH) GmbH & Co. KGaA.) concerning the International Year of Light has been published. Herein the author Thorsten Bach asks: „Why is chemistry overlooked when talking about light? Is the photon a physical particle per se? Are all important light-induced processes biological? And his answer is: „Maybe the role of light for chemistry and the role of chemistry for light may be far less important than a few eccentric scientists would like to believe. From the perspective of a synthetically oriented photochemist, however, the facts are different”.

Photochemical processes hold indeed key functions not only within demanding syntheses in organic chemistry but also in the conversion of solar radiation into storage of chemical energy following the role model of natural photosynthesis. This is even true for the photovoltaic conversion of light into electric energy and vice versa, namely the efficient conversion of electric energy into light as in LEDs and OLEDs. Photochemistry is involved in all these and many other processes, because the electronic excited state can be seen as a defined chemical species with totally different properties as the ones assigned to the ground state. Nick J. Turro already expressed this point of view in 1978: „The excited state is in fact an electronic isomer of the ground state"and he also concluded „The ‚photo" part of molecular photochemistry is a historical prefix and is now too restrictive. It is now clear that the electronically excited states of molecules are the heart of all photoprocesses."

We chemists are well informed about the structure and properties of material entities, e.g. the molecules. And what do we know about the photons, the entities of light? Albert Einstein admitted a few decades after his Nobel Prize work of the annus mirabilis from 1905 about the photoelectric effect: „Zwanzig Jahre meines Lebens haben mich der Antwort auf die Frage ‚Was sind Lichtquanten' nicht näher gebracht. Heute bildet sich jeder Wicht ein, er kenne die Antwort. Doch da irrt er." (Twenty years of intensive thinking haven't brought me any closer to the answer of the question what a photon really is. Today every simpleton thinks he knows the answer, but they are mistaken.) It is known today that Albert Einstein had been speculating about the nature of photons (light quanta) without ever finding a definite meaning. Well, one is such a simpleton, if one goes into philosophical speculations about the nature of light quanta. However, as a pragmatic chemist one can tread on safe terrain by interpreting photons in the sense of Max Planck simply as the smallest packages of energy of electromagnetic radiation. Colloquially speaking it can be said, that photons assume the same role within the „zoo" of radiations as atoms, ions and molecules do within the „zoo" of matter, namely being the smallest portions or the smallest particles. Furthermore it can be added that certain photons can be absorbed or emitted by certain particles. This explanation would be really simplified but intelligible. With the basic concept of the ground and excited states all processes in which material entities and photons are involved can be described and explained in a at first simplified but scientifically consistent way. In that way the demand of „More Light! In Chemical Education Too!" as found in the editorial of the editorial of the CHEMKON (4/2015), GDCh-journal of the Division Chemical Education, can be satisfied.

Go online!

Many exciting innovations and discoveries are made at the interface where chemistry

meets the other sciences. This fact is undisputed and photochemistry offers many prototypical examples. Molecular switches, biological

imaging, organic light-emitting diodes, photodynamic therapy, functional dyes, photovoltaics: the keyword list for important interdisciplinary topics in photochemistry is long and keeps growing.
In order to provide large information, the Gesellschaft Deutscher Chemiker (GDCh; German Chemical Society) has established are very well-produced websites related to the International Year of Light. For example, a project coordinated by Axel G. Griesbeck and Renate Hoer was collecting and publishing online each week in 2015 excellent contributions that cover all facets of the interaction between chemistry and light. This site can be found in a section called Aktuelle Wochenschau on www.aktuellewochenschau.de/main-navi/startseite.

The GDCh-Divisions „Photochemistry“ and „Chemical Education“ have designed the website www.iyl2015.uni-wuppertal.de containing a large variety of information about conferences, symposia, lectures and workshops during the year 2015 as well as a collection of Youtube videos from scientists working in the field of photochemistry and different teaching materials for photochemistry. It’s worthy to emphasize the respectable number of experiments (more than 50), the two experimental boxes Photo-Mol and Organic Photo Electronics (see below) and the interactive animations simulating elementary processes with participation of light. Since the iyl-website indicated above is basically edited in German, we advise also www.chemiedidaktik.uni-wuppertal.de/ english that contains materials in English. These sources for online information will be available even after the end of 2015.

Photochemistry in Basic and Applied Research

Basic and Applied Photochemistry in a large variety is represented by scientific groups affiliated to GDCh-Division Photochemistry. Their research seeks for deeper understanding of photoprocesses as well as for new applications involving light. In 2015, more than 60 colleagues from academia, industry and science education reported on their activities in these fields by easily readable contributions that are published online in the GDCh forum "Aktuelle Wochenschau". A collection of these contributions is given here (only the corresponding authors are listed here):

Contributions from chemistry eduction:
Renate Hoer, „Millions of light at the ACHEMA 2015 in Frankfurt"
Judith Rahner,"Organic Photovoltaics at the EXPO 2015 in Milano"
Michael Tausch, „Chemistry and Light: an imperativ for education and teaching"
Claudia Bohrmann-Linde, "Liquid Crystals – experiments for teaching"
Amitabh Banerji, "OLED.Education"
Axel Griesbeck, "History of photochemistry"
Oliver Happel, "OLED-photometer for chemistry education"
Daily life phenomena:
Reinhard Zellner, "The earth atmosphere – a photochemical reactor"
Axel Griesbeck, „Blood analysis with chemoluminescence"
Axel Griesbeck, „Oxygen: Dr. Jekyll and Mr. Hyde"
Martina Neises-von Puttkammer, "Solar fuels from water and carbon dioxide"
Organic and Inorganic Photochemistry:
Burkhard König, "Organic synthesis with visible light"
Thorsten Bach, "Chirality and Light"
Horst Kisch, "Semiconductor as Photocatalysts"
Horst Hartmann, "Fluorescent organic nanoparticles"
Axel Griesbeck, „Photochemical protecting groups"
Karola Rück-Braun, "Photochromic organic molecules"
Michael Oelgemöller, "Solar Photochemistry"
Biological and Medicinal Chemistry:
Percy Lehmann, „Photodynamic Therapy"
Christoph Bräuchle, „High-resolution light microscopy for tumor therapy"
Kathrin Freudenberger, "Optical Sensors in medicinal diagnostics"
Physical Chemistry and Spectroscopy:
Peter Gilch, „Femtochemistry"
Christoph Haisch, Photoacoustic spectroscopy"
Dirk M. Guldi, „Singlet fission – make two out of one"
Maria Wächtler, "Following photoinduced catalysis with laser light"
Applied and Analytical Chemistry:

Gerhard Schlemmer, „Chemical analytics with light“
Axel Klein, „Photoinduced liberation of small molecules and radicals“
Michael Oelgemöller, “Flow Photochemistry”
Klaus Wendt, “Ultratrace analysis with laser light”
Thomas Oppenländer, “Sustainable detoxification of water”
Wolfgang Schnick, “White LED´s – High performance light sources”
Uwe Karst, “(Bio)imaging of elements by LA/ICP-MS”
Michael Schmidt, “Spectral and absolute calibration of light sources”
Alexander Kühne, “Switchable colored materials and future applications”
Wolfgang Buscher, “Plasma-spectroscopy, Part I and II”
Bernd Strehmel, “Light sources for lacquer chemistry: from UV to IR”
Claudia Weidenthaler, “Investigation of porous catalysts with light”
Contributions from industry:
Michael Dreja, „Can we enlighten our laundry?“
Brigitte Dicke, “Color: from vision to code numbers”
Heinz Mustroph, “Agfa and the beginning of industrial photography”
Adalbert Huber, “Effect pigments for optical effects in paints lacquers”
Thomas Fäcke, “Holographic photopolymers for diffractive optics application”

Further aspects of topical photochemistry and related areas (photobiology, photomedicine, spectroscopy and applied photosciences) were and will be covered also at symposia organized and sponsored by the GDCh such as the Wissenschaftsforum 2015 (WiFo) in Dresden, the regular scientific meetings of the photochemistry division of the GDCh (2014 in Cologne, and 2016 in Jena) as well as the Central European Conference on Photochemistry (CECP 2016 in Bad Hofgastein). During the WiFo2015 a session on synthetic organic photocatalysis was organized as a side-program to the plenary lecture of Stefan Hell, the 2014 Nobel laureate in Chemistry. Numerous lectures on all aspects of photochemistry and the educational aspects of photochemistry were also presented by the members of the Divisions of photochemistry and chemistry education of the GDCh.

Photoprocesses in Science Education

Due to the omnipresence of photoprocesses in nature and life as well as their large technical applications these phenomena nowadays count among the everyday experiences of everyone. Nevertheless they count also among the topics in scientific research at the highest level. Note for example that the Nobel Prices in Physics and Chemistry 2014 have been awarded for the blue LEDs and for the STED-Nanoscopy.

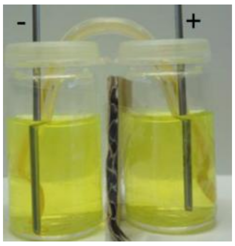
It should be emphasized that from the educational point of view photoprocesses are par excellence suitable for teaching several basic concepts of chemistry, physics, biology, informatics, geography and further disciplines in close combination with everyday experiences and convincing applications from science and technology in the 21st century. Therefore research in chemical education is challenged to investigate and develop teaching materials for the inclusion of photoprocesses into science education. In this sense a couple of members and groups from the GDCh-Division Chemical Education are doing pioneering work in collaboration with the GDCh-Division Photochemistry.

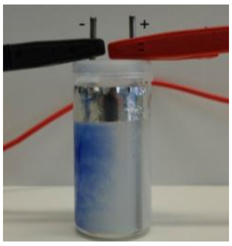
The declaration of 2015 by UNESCO as "International Year of Light" pushed them once more to intensify their activities. The strategic focus of these activities is the investigation of experimental approaches for core concepts concerning first of all photoprocesses, but generally applicable in chemistry and related scientific disciplines. Common concepts for all chemical phenomena such as the relation between the structure of particle and the property of matter and donor-acceptor concept can be applied one-to-one for photochemical processes too. Other concepts, for example those regarding redox reactions, catalysis, kinetics, chemical equilibrium, and chromaticity have to be adjusted to the situation of the electronically excited state, the "heart of all photoprocesses".

A series of novel experiments and teaching materials have been developed for investigating following photoprocesses: fluorescence and phosphorescnece, electro- chemo- and electrochemoluminescence, photo-, solvato- and electrochromism, photovoltaics in inorganic, organic and hybrid cells, photocatalytic redox reactions in homogeneous and heterogeneous systems, photoisomerisations and photosteady states in solutions and in rigid matrices.

A considerable number of these experiments have been combined into two experimental boxes. The Photo-Mol box (photones and molecules) contains as light sources LED flash lights for white, violet, green and red light. The main chemicals are aesculin (for fluorescence and phosphorescence experiments) and spiropyrane. This is a veritable dream compound for teaching not only photo- and solvatochromism but also the basic differences between the thermal and photochemical reactions and also the difference between a thermodynamic equilibrium and a photosteady state. A central experiment in the Photo-Mol box is the preparation and investigation of an „intelligent foil“ with the molecular switch spiropyrane/merocyanine embedded in a solid matrix of polystyrene. The major part of the instruction book are 23 worksheets for the interpretation and theoretical explanation of experimental observations at different teaching levels starting from the lowest level in chemical education up to the high school and even to the university level. The book and the USB stick contain, additionally to the worksheets, supplemental information about experiments, safety instructions, advice for the teacher and electronic materials, such as videos and model animations. Since July 2015 the Photo-Mol box is provided by the Hedinger Company Stuttgart. The English translation of the instruction book is still projected, nevertheless English materials are already available online via www.chemiedidaktik.uni-wuppertal.de/english.

The OPE box (organic photo electronics) contains equipment for assembling OLEDs and OPVs (organic photovoltaic cells). For this several quite expensive materials and chemicals are needed, i.e. conductive FTO (fluorine doped indium-tin-oxide) glass, galinstan (liquid alloy of gallium, indium and tin), „superyellow“ (a derivative of poly-para-vinylene-phenylene), P3HT (poly-3-hexyl-thiophene), PCBM (phenyl-C61-butyric acid methyl ester) and PEDOT:PSS (poly-ethylendioxythiophene, poly-styrenesulfonate). However, an ingenious and very cheap spin coater has been conceived. It is used for applying thin layers of photoactive materials on the FTO glass for both devices, for OLEDs as well as for OPVs. The OPE instruction book is designed similar to the Photo-Mol book discussed above. Up to the end of 2015 it will be available in German and English. Nevertheless, the OPE box is not yet provided commercially, it is still in the testing and evaluating phase. Note, that very detailed online materials for assembling and investigating OLEDs and OPVs are already available for free in German, English and Spanish via the iyl-website cited above.



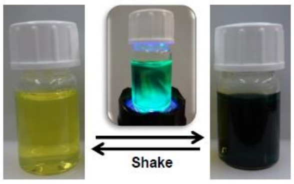


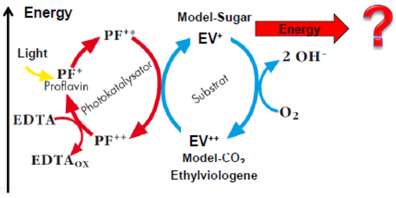
During 2015 the experiment called Photo-Blue-Bottle PBB simulating the natural cycle of photosynthesis and respiration has been rigorously improved for teaching purposes. It is now available in a microscale version operating with non-hazardous chemicals (nontoxic ethylviologen instead of toxic methylviologen) und low-priced light sources (LED flash lights). The light driven reduction of the substrate can now be realized in homogeneous solution with proflavine as photocatalyst as well as in a suspension with nano-TiO2 (anatas). The conversion of light into chemical energy and storage in the reduced substrate until the reoxidation can be simply demonstrated in a concentration cell with irradiated and non-irradiated PBB solution or suspension respectively.

Details on the PBB experiment including theoretical background and advice for teaching photocatalysis are available online via www.chemiedidaktik.uni-wuppertal.de/english/index.html (see “Workshop” in Valencia and “Scientific Lecture” at SEADIM conference in Varadero, 2015). According to the actual topic in scientific research and development related to the age “Behind CO2 Capture and Conversion” the PBB experiment became additionally relevant as teaching model for the endergonic and photocatalytic reduction of a substrate using sunlight as driving force.

Since several years we have been engaged in the transfer, communication and evaluation of teaching materials that involve photoprocesses to students, school teachers and academic lecturers. Encouraged by the Energiewende proclaimed in Germany we have been intensifying our efforts. Alone during the “International Year of Light 2015” more than fifteen experimental lectures, workshops and teacher training events have been given, for example in Frankfurt, Hannover, Berlin, Potsdam, Munich, Darmstadt, Wuppertal, Erfurt, Dresden, Aachen, Siegen, Rostock, Innsbruck, Havana, Varadero and Valencia. As expected, it has been found that the participants became highly motivated for dealing more and deeper with photoprocesses. This applies not only for people interested in chemistry, but also for those more oriented towards physics, biology, informatics and terrestrial atmosphere.

In the future educational programs and syllabi have to pay more importance to photoprocesses. Accordingly pretty experiments and the basic concept of the ground state and electronically excited states should be included and connected with the well-established concepts in the textbooks for teaching and learning chemistry in high schools





and universities. Doing so, we could essentially improve and accelerate the development of techniques for overcoming the "big five" global challenges of the 21st century related to the terms of energy, food, water, climate and mobility.

We like to acknowledge GDCh, DFG, FCI and Merck Darmstadt for supporting the investigation and the development of experiments and teaching materials discussed in this report.

Photo-Chemistry! Light, environmental monitoring and cancer fighting

A hands-on workshop for 11th grade high school students in the International Year of Light 2015

Guillermo Orellana
Chemical Optosensors & Applied Photochemistry Group (GSOLFA), Dpmt. of Organic Chemistry, Faculty of Chemistry, Complutense University of Madrid (UCM), 28040 Madrid (Spain)

On the occasion of the XVth Madrid Science Week (Nov. 2015), the UCM Chemical Optosensors & Applied Photochemistry Group (www.gsolfa.info/en) led by Prof. Orellana, organized a lively Workshop to teach junior high school students how light-induced chemical reactions (Photochemistry) is currently helping to improve our quality of life. Two areas that illustrate how photochemists have "domesticated" photons were addressed in three different hands-on experiments dealing with water quality monitoring (with luminescent chemical sensors) and cancer fighting (with photodynamic therapies).

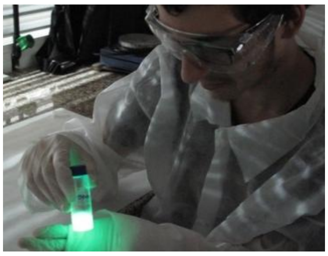
The Workshop was repeated for three days (Nov. 4-6), in ca. 2-hour sessions for 45 students per day within the organic chemistry laboratory. In each session, after a 10 min general introduction by the activity organizer, the students were divided into 3 groups, and two tutors (GSOLFA PhDs and postdocs) per group taught them the basics of each topic and helped them to carry out the planned experiments.

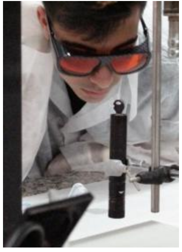
Dr. Maxi Bedoya and Guido Ielasi educated the attendees on how photochemical luminescent sensors based on optical fibres are used nowdays to monitor in situ, continuously and in real time, important water quality parameters such as the dissolved oxygen level. They showed the students how to manufacture a real sensor using an ordinary silicone sealant and a Ru(II)-polypyridyl indicator dye. After they prepared themselves such a sensor, the students tested the amazing red-orange luminescent O_2-sensitive films under the uv light before and after being hit with a focused nitrogen gas stream.

Dr. Victoria González de Vallejo and Idoia Urriza taught their pupils the applications of chemiluminescence to toxicity testing of natural waters and personal safety. Delivering to the students different fluorescent dyes, they prepared awesome “light sticks” by mixing the dyes with diaryloxalates and hydrogen peroxide solutions.

Francesca Salis, José Angel de la Torre and Dr. Pramiti Hui illustrated the students the working principle of photodynamic therapies based on the reactivity of singlet molecular oxygen ($^1O_2$) to heal cancer and other diseases. Without using any real cell culture, the students discovered the effect of $^1O_2$ photosensitizing dyes on simulated tumours, upon violet diode laser or He-Cd laser excitation.

Both students and tutors enjoyed three days of rewarding interaction to celebrate the IYL2015, wishing they had had more time to learn the thrilling applications of Photochemistry!





Workshop on Photochemistry (International Year of Light 2015)

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Light-driven technologies are continuously emerging for applications that would offer new improvements to our quality of life. New photovoltaic devices, biomedical applications, fighting counterfeiting, and self-cleaning materials are just a few examples of the impact than light responsive materials can have in our lives.

In this context, it is a must to attract the attention of the general public and also students who will be part of the next generation involved in new discoveries based on light-matter interactions. Undoubtedly, the organization of outstanding activities on the occasion of the International Year of Light is an excellent opportunity to engage students and researchers in this topic. For this reason, the Photochemistry Reactivity Group[1], led by Prof Pérez-Prieto, hosted a Workshop on Photochemistry (Fig. 1). This highly pedagogical workshop was directed towards senior undergraduate and junior graduate students from chemistry, physics, engineering, and the life sciences. The workshop took place on October 14th, 2015 together with the celebration of the 17th Science Week at the University of Valencia. This was possible thanks to the outstanding and passionate contribution of Michael Tausch, Claudia Bohrmann-Linde and Amitabh Banerji from the University of Wuppertal, who have an excellent background in chemical education (mainly in the field of photochemistry) and also thanks to the organization and dissemination of the activities from the Scientific Culture and Innovation Unit Chair for Scientific Dissemination from the University of Valencia. The topics ranged from basics of photochemistry to conversion of electricity into light and *vice versa*.

The welcome and opening of the workshop by Prof Pilar Campins (Vice-rector for Research), Prof Isidro-Salvador Monzó Mansanet (*Dean of the Faculty of Chemistry)* and Prof Julia Pérez Prieto was followed by three interesting, didactic and communicative lectures during the morning session that included demos given by Prof Tausch and colleagues.[2-4]

After lunch, students were strongly encouraged to participate in three hands-on sessions designed by the University of Wuppertal team, alternating with another three experimental demos that included, for example, forensic chemistry and chemiluminescence experiments organized by Soranyel González Carrero and carried out by the University of Valencia team.

At the end of each session, the monologist Mariano Collantes talked about how we can communicate with bacteria using light and transgeneses.[5]

The excellent educational atmosphere created between the students and those giving the lectures and carrying out the demos was even better than we hoped for.

The workshop was held in English and enrolment was limited to 100 participants to ensure involvement in the hands-on experiments and keep the students' attention focussed on the topic. For those who already had some experience in photochemistry, the workshop improved their knowledge and techniques through lectures and hands-on training offered during the sessions. For those who were interested, but new to the topic, the workshop was an excellent opportunity to start them off in this field.

For more information about the workshop, please go to the website and Youtube video below.
http://www.uv.es/uvweb/unitat-cultura-cientifica-innovacio-catedra-divulgacio-ciencia/es/unitat-cultura-cientifica-innovacio-catedra-divulgacio-ciencia/oberta-inscripcio-workshop-fotoquimica-1285898622434/Novetat.html?id=1285948568367
https://www.youtube.com/watch?v=dNJX59Opg-Y

Figure 1. Flyer announcing the Workshop on Photochemistry at University of Valencia and two photos taken during the lectures.

<u>Other activities</u> – This year the *Institute for Molecular Science (ICMol) of the University of Valencia* is holding its 15th Scientific Conference dedicated to the International Year of Light with informative lectures on photochemistry on Friday December 11th. Three lectures will be given "Molecules and light: Applications in Materials Science and Medicine" by Prof Luisa De Cola from *Institut de Science et d'Ingénierie*

Supramoléculaires, Université de Strasbourg, who was awarded the binational Catalán Sabatier 2015 Prize by The Real Sociedad Española de Química; "Molecular solar cells based on perovskites: A real alternative to the silicon cells?" by Prof Khaja Nazeeruddin from *Ecole Polytechnique Federale de Lausanne,* and "Luz, química y vida" by Prof Miguel Ángel Miranda from *Instituto de Tecnología Química, CSIC/UPV.*

Remarkably, last May, The University of Valencia Science Park (PCUV) organized Expociencia (seventh edition), which is a relevant scientific activity, under the slogan "May science light you" to commemorate the International Year of Light.

Acknowledgment – The Photochemistry Reactivity Group thanks Michael Tausch, Claudia Bohrmann-Linde, and Amitabh Banerji from the University of Wuppertal and the Scientific Culture and Innovation Unit Chair for Scientific Dissemination from the University of Valencia, and the funding agencies that made the workshop possible.

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The International Year of Light – a Personal and Professional Perspective

Malcolm D. E. Forbes, President, Inter–American Photochemical Society 2014–2016, Director, Center for Photochemical Sciences, Bowling Green State University, Bowling Green OH, 43403, forbesm@bgsu.edu

The 24th Winter Meeting of the Inter–American Photochemical Society took place in Sarasota, Florida January 1–4, 2015. This conference unofficially marked the first professional photochemistry event in UNESCO's International Year of Light (IYOL) and Light Technologies. Some of you may remember me lighting a candle at the meeting to make our "inaugural event" somewhat more official, and to commemorate the IYOL as a Society.

Our 2015 meeting, put together by co–organizers Sivaguru Jayaraman (North Dakota State University) and Clemens Burda (Case Western Reserve University) was a great success, with over 100 attendees and a very high quality scientific program in addition to some excellent weather, which was especially welcomeat our new banquet site, *Tommy Bahama's*. The lecture sessions included presentations by many I–APS Award winners: There were two Gerhard L. Closs student travel awards (Elango Kumarasamy of North Dakota State University and Albert King of Ohio University). Josef Michl of the University of Colorado received the second ever Hammond award, Claudia Turro of the Ohio State University was the recipient of the 2014 I-APS Award in Photochemistry, and Joel Rosenthal (University of Delaware) was our 2014 I–APS Young Investigator. In addition, we inducted two I–APS Fellows: Richard Givens of the University of Kansas, and Frank Quina of the University of Sao Paulo, Brazil.

Throughout 2015, I experienced my own personal Year of Light, not only as current President of I–APS, but also as co–Chair (with Anna Gudmundsdottir of the University of Cincinnati) of the 2015 Gordon Research Conference on Photochemistry, which was held at Stonehill College in Easton, Massachusetts in July. This conference was attended by almost 150 scientists from across the globe and was also a great success. Most importantly, in July 2015 I made a professional move from the University of North Carolina at Chapel

Hill, where I had been a Chemistry faculty member for 25 years, to take the position of Director of the Center for Photochemical Sciences at Bowling Green State University in Ohio. My move has made 2015 an exciting year, full of transition and new momentum for my research group, my family, and myself. I am now very happily settled in northwest Ohio, running a vibrant Center that is a unique entity: the only institution in the world that offers a doctoral degree in the photosciences.

My most visible contribution to the IYOL is an *Outlook* I wrote for the newest journal from the American Chemical Society (ACS Central Science), entitled "What We Talk About When We Talk About Light."[1] The paper, about which I have received many comments (not all of them complementary), is unconventional in that it attempts to provide a history of light from the first moments of the Big Bang up to the present day, and then pontificates about some interesting new research directions that I hope will stimulate young researchers in the field.

It was not easy to start with the Big Bang and arrive just a few pages later at technological advances such as the Edison light bulb and the laser. Early versions of the paper also included a more holistic view of light, detailing some of its roles in sociological anthropology (e.g., the gathering of early humanoids around campfires), politics (e.g., the first use of television in political debates in 1960), and religion (the use of stained glass and beeswax candles in Rennaissance churches, and the activities of the sun worshippers of Stonehenge are notable examples) (Figure 1). It is probably fortunate that the wisdom of the editors prevailed as these musings were trimmed from what was supposed to be a scientific paper, but nonetheless they were interesting to think about.

In addition to technological marvels in light such as the Fresnel lens for lighthouses, the Nd:YAG laser for surgery, and most recently, the tremendous advances in resolution byond the Abbe limit in optical microscopy, there are two major 20th Century thrusts in fundamental science that provided a detailed understanding of light in nature: the mechanisms of photosynthesis and vision. Through a Herculean effort by chemists, physicists, and biologists, the process of photosynthesis from the moment a photon hits the surface of a leaf to the production of a single molecule of ATP is now very clearly understood in terms of thermodynamics, reactive intermediates, and rate constants. There is still a way to go before we are able to

Figure 1. Light outside the scientific laboratory. Clockwise from top left: the first Kennedy–Nixon debate (September 26, 1960: note the contrast of Kennedy's dark suit against the grey background compared to Nixon's), a piece from artist Jan Tichy's "Politics of Light" exhibition (2013), the map room from "Raiders of the Lost Ark (1981)", Stonehenge at sunset (photo by Jake Rosen).

duplicate the necessary features for sustainable artificial photosynthesis, which is a major goal in current energy and agriculture research. A detailed molecular understanding of vision is also at hand, which has in turn led to interesting advances in brain function and memory. Electronic implants to provide visual ability for blind humans and other animals are now a reality, and represent an exciting step forward in this field.

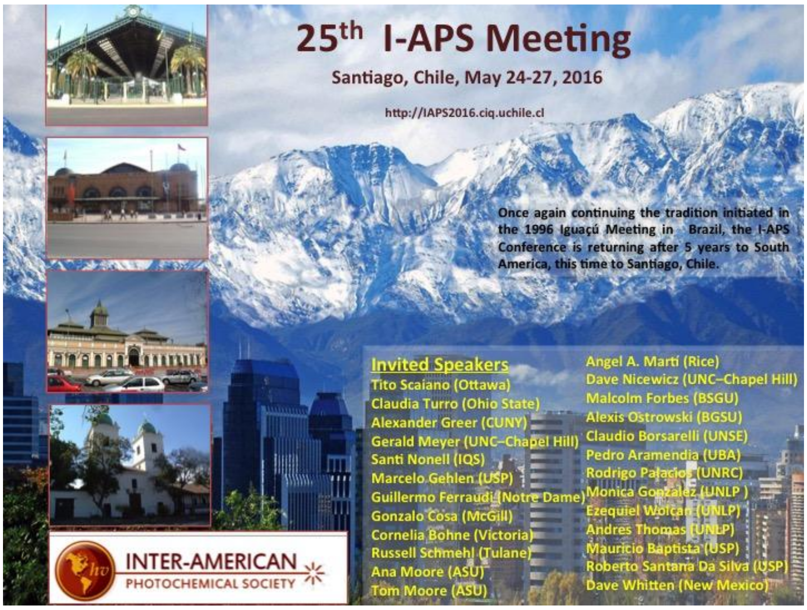
This *Outlook* provided a platform to point out a few research areas that I thought would grow significantly in the next thirty years, to help guide younger scientists as they venture into independent research. My list of topics was by no means comprehensive – if a particularly exciting area was omitted, I am happy to learn of it. Remember that prediction is difficult, especially of the future!

So what is my opinion of that future? Societal issues such as management of energy resources, feeding a growing population, and protecting our planet's fragile ecosystems are all high priorities that will demand a significant research effort to address. Finding thermal or photochemical pathways for the reduction of CO_2 to other reusable carbon feedstocks will not only contribute to alternative and cleaner energy technologies, but might also enable sequestration of atmospheric CO_2 and, as hinted above, provide insight into methodologies for artificial photosynthesis to provide nutrients for humans as well as other plants and animals. Fluorescence microscopy and other biological imaging techniques will transform modern medicine, and I have already mentioned artificial vision, which will extend into neuroscience as we try to understand the role of the optic nerve and pattern recognition processes in the brain. The use of quantum dots and other more sophisticated nanostructured devices for medical, agricultural, and energy advances will continue to accelerate. A looming problem is phophorus runoff from agricultural fertilizers which, in addition to accelerating depletion of the world's minable phosphorus supply, is now known as a major contributor to algae blooms (e.g. in Lake Erie in the U.S.) that can choke ecosystems almost completely and have proven to be harmful to humans in some cases. A method for returning phosphorus from lakes and oceans to useful fertilizer, perhaps using photochemical energy form the Sun, is a 21st Century "Holy Grail" in the field of agriculture.

I also used this paper to drive home a particular point about interfaces and how poorly understood they are from a molecular perspective. There is a great deal of room here for advancement and light can play a large role in this field. My criticism centers on the following comment: everything in the universe is interfaced in some fashion with everything else. But the types of interfaces that have been probed spectroscopy, and the variety of techniques used, has led to a scattering of data so large and seeminlgy divergent that what is learned from one study becomes almost impossible to generalize or to correlate with another. I likened the problem to the situation that existed in the field of electron transfer before Closs and Miller performed their systematic experiments on what we now call Donor–Spacer–Acceptor molecules.[2] This "physical organic chemistry" approach is exactly what the field of interfacial science needs in order to better understand, for example, bonding motifs of catalysts on semiconductors for solar fuels production. Optimization of the efficiencies of such devices will not be possible without such a detailed understanding.

The most interesting comments I have received about the paper were focused on my closing quote from Thomas Wolfe's *Look Homeward, Angel*, which many readers seemed unable to connect to the overall content. If you are curious, I encourage you to read the paper and see if you can connect the dots to Wolfe's rather obtuse quote (hint: think in the abstract rather than the absolute). Please feel free to email me your thoughts!

In closing, I would like to extend an invitation to all of you to attend the 25th I–APS Meeting to be held in Santiago, Chile May 24–27, 2016 (Figure 2). After four previous conferences in South America, this marks the first time that our meeting will be held in Chile, and the organizers have put together a fantastic program in a beautiful location. I encourage you to join us there for what is sure to be a great meeting: http://IAPS2016.ciq.uchile.cl



25th I-APS Meeting

Santiago, Chile, May 24-27, 2016

http://IAPS2016.ciq.uchile.cl

Once again continuing the tradition initiated in the 1996 Iguaçú Meeting in Brazil, the I-APS Conference is returning after 5 years to South America, this time to Santiago, Chile.

Invited Speakers

Tito Scaiano (Ottawa)
Claudia Turro (Ohio State)
Alexander Greer (CUNY)
Gerald Meyer (UNC–Chapel Hill)
Santi Nonell (IQS)
Marcelo Gehlen (USP)
Guillermo Ferraudi (Notre Dame)
Gonzalo Cosa (McGill)
Cornelia Bohne (Victoria)
Russell Schmehl (Tulane)
Ana Moore (ASU)
Tom Moore (ASU)
Angel A. Martí (Rice)
Dave Nicewicz (UNC–Chapel Hill)
Malcolm Forbes (BSGU)
Alexis Ostrowski (BGSU)
Claudio Borsarelli (UNSE)
Pedro Aramendia (UBA)
Rodrigo Palacios (UNRC)
Monica Gonzalez (UNLP)
Ezequiel Wolcan (UNLP)
Andres Thomas (UNLP)
Mauricio Baptista (USP)
Roberto Santana Da Silva (USP)
Dave Whitten (New Mexico)

Figure 2. Advertisement for the 25th Inter–American Photochemical Society Meeting in Santiago, Chile in 2016.

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The International Year of Light and Light-based Technologies 2015 in Italy

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Lots of initiatives, at various scales and levels, took place throughout Italy to celebrate YIL 2015. Of course, it would be impossible to mention all of them;[1] here we will briefly present the main events organized with the contribution or the involvement of the Italian Group of Photochemistry (http://www.fotochimica.org) and the Italian Chemical Society (http://www.soc.chim.it).

"Luci sullo stretto" (Lights on the strait). Messina, 30 March, 13 April and 20 April – This public event[2] was set up by the University and the City Council of Messina in cooperation with the Italian Group of Photochemistry. The role of light in several areas of science, technology, philosophy and religion was discussed in twelve conferences held by national experts. Overall, more than 2000 people attended the conferences during the three days.

Avogadro Colloquia "Chemistry and light". Rome, 22 May – This one-day public symposium was organized by the Italian Chemical Society in the frame of the "Avogadro Colloquia" meetings.[3] First-class researchers illustrated in conference and round tables the major challenges in the context of chemistry and light, with particular focus on a number of areas of application with remarkable societal impact, including medicine, energy, and environment.[4] In consideration of the central role of Italy in world cultural heritage, the closing session was focused on the combination of chemistry and light for the enhancement and preservation of artistic masterpieces. At the end of the meeting, the participants had the chance to visit the beautiful Sistine Chapel, Vatican Museums, and enjoy the new LED-based lighting system.[5]

"Bologna s'illumina" (Bologna lights up). Bologna, 9-14 November – Several national and local institutions, including the University of Bologna, the National Institute for Astrophysics, the Italian Physical Society and the Italian Group of Photochemistry, in cooperation with

the Fondazione Marino Golinelli, organized one week full of meetings with scientific experts and VIPs, laboratories, exhibits and shows open to students of all ages as well as to the general public (Figures 1 and 2).[6]

Figure 1. *Bologna s'illumina.* Top: opening ceremony in the beautiful setting of the Archiginnasio Palace on 9 November. Bottom: Laboratory activities with primary school students at the Opificio Golinelli on 11 November.

The topics spanned from physics to biology and from astronomy to chemistry, also touching arts and social sciences. The program included a training course for teachers entitled "The thousand faces of light in astronomy, chemistry and physics". Among the various shows, "The journey of Joe the Photon: a blues story" was particularly successful, while it is worth mentioning the laboratories about "Chemistry in colors", "Playing with light: from visible to invisible", "Light and the world of plants" and "Light and atoms". Overall, more than 4000 people attended the various events of the initiative.

Figure 2. *Bologna s'illumina.* Left: light effects on the facade of the Santa Lucia Main Lecture Hall of the University of Bologna on 13 November. Right: musician and writer Roberto Vecchioni, physicist Luisa Cifarelli, photochemist Vincenzo Balzani and astrophysicist Fabrizio Bignami discuss about light, science and life with actor and showman Patrizio Roversi, in front of an audience of several hundreds people.

Other contributions and activities – In their essay[7] opening the issue of *Angewandte Chemie International Edition* dedicated to the International Year of Light (n. 39, vol. 54, September 2015), Vincenzo Balzani, Giacomo Bergamini and Paola Ceroni pointed out that light is a very peculiar reactant and product in chemical processes. This important concept is commonplace for photochemists but it is certainly worth to be emphasized for the wider chemical community.

The following scientific conferences and schools dealing with chemistry and light took place in Italy in the frame of IYL 2015: *National School of Physical Chemistry "Energy production, storage and conversion"* (Otranto, 8-12 June),[8] *Workshop "Chemistry, Materials and Light"* (Bologna, 21-23 September),[9] *New Trends in Organic Synthesis* (Milan, 30 November),[10] and the *Italian Photochemistry Meeting 2015* (Bologna, 17-19 December), which is the annual meeting of the Italian Group of Photochemistry.[11]

Other events for the general public included the round table *"Fiat Lux. Is a world without light possible?"* within the first world reunion of the University of Bologna Alumni (19-21 June)[12] and a series of conferences, shows, exhibits and laboratories entitled *"La luce... come non l'avete mai vista" (Light... as you have never seen it)* organized in Parma by the City Council, the University and the National Research Council from October 2015 to January 2016.[13]

Such a plenty of initiatives for IYL 2015 in connection with Chemistry highlight the excellent health of Photochemical Sciences in Italy and reflect the intense scientific research and teaching activities going on in this area. The strong effort to make these events possible and the wide participation of the public are key to continue the long standing Italian tradition in Photochemistry[14] established since the times of Emanuele Paternò and Giacomo Ciamician.

Acknowledgment – The author thanks all the members of the Italian Group of Photochemistry (GIF) and of the Photochemistry section of the Italian Chemical Society (GIdF) for their invaluable contribution to the development, promotion and divulgation of Photochemical disciplines in Italy. INFN and Opificio Golinelli are gratefully acknowledged for providing the photographs.

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New Trends in Photochemical Engineering and Technologies

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In recognition of the **'International Year of Light and Light-based Technologies (IYL 2015)'**[1] the journal *Chemical Engineering & Technology (CET)* published a dedicated special issue on *'New Trends in Photochemical Engineering and Technologies'* in January 2016.[2] The cover features the IYL logo together with a spiral-shaped capillary microreactor developed by Loubiere and co-workers (Figure 1). The device allowed for *in-line* reaction monitoring by UV-Vis spectrophotometry and was used to study a photochromic reaction.

Figure 1. Front cover of the special issue of CET.

Associate-Professor Michael Oelgemöller from James Cook University and Dr Karine Loubiere from the Université de Toulouse served as guest-editors. The special issue comprises 5 review papers and 13 research articles from across the world. The 18 contributions highlight new photoreactor systems and light sources, photoreactor modelling, photochemical methodologies and photoactive materials.

Strehmel et al. review digital imaging of lithographic materials by radical photopolymerization and photonic baking with NIR diode lasers. Lacombe and co-workers review reactors and materials used in gas-phase photooxidations for air treatment. Lomaev and colleagues present a review on excilamps and their applications in photochemistry. De Lasa describes photocatalytic efficiency evaluations using quantum yields and the photochemical thermodynamic efficiency factor. Rehm reviews photochemical fluorination reactions under continuous flow conditions. Oelgemöller et al. study photodecarboxylation reactions in an advanced continuous flow-reactor und furthermore apply it to the synthesis of a biological active target compound via a photo-thermal tandem process. Liu and collaborators develop a planar photocatalytic microreactor and assess its efficiency to degrade methylene blue. Li and co-workers utilize a microwave discharge electrodeless lamp in combination with H_2O_2 for the photooxidation of guaiacol to potentially valuable carboxylic acids. The group of Horikoshi develops solar-powered microwave discharge electrodeless lamps and utilizes them for continuous on-site field treatment of contaminated water. Deng uses computational fluid dynamics to assess radiation fields and disinfection efficiencies in UV reactors. Modelling and experiments in a spiral-shaped LED-driven microreactor are performed by Loubiere et al. to acquire kinetic data on a photochemical system. Ziegenbalg and his group study photon fluxes inside micro-structured photoreactors to demonstrate further optimization needs for these devices. Ponce-de-Leon and co-workers describe the construction of a photocatalytic flow reactor for the oxidation of methyl orange. Taghipour and Adeli report on the development of a GaN:ZnO-reduced graphene oxide composite for water splitting. Likewise, Fazaeli and colleagues design CdS and Ag/CdS nanoparticles for photocatalytic azo dye degradation. Hermosilla and collaborators describe the effects of carbonates on TiO_2-photocatalysis and photo-Fenton processes. Likewise, a commercially available TiO_2 photocatalyst doped with carbon is used by Ballari et al. for the degradation of acetaldehyde as an air pollutant.

Finally, Landgraf utilizes semiconductor light sources for time-resolved fluorescence HPLC detection.

Overall, the content of this special issue clearly demonstrates the importance of 'light' in applied photochemistry and photochemical engineering.

Acknowledgment – The authors thank Dr Elmar Zimmermann (deputy editor) and Dr Barbara Böck (editor in chief) of Chemical Engineering & Technologies for supporting this special issue.

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PILLS OF HISTORY

At the origin of photochemistry. Leone Maurizio Padoa

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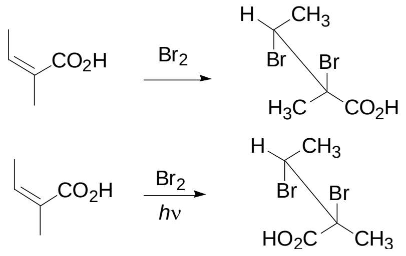
Maurizio Leone Padoa was an assistant of Giacomo Ciamician. Usually, most of the photochemical work on photochemistry was performed by Ciamician with the help of Paul Silber, and we know all on this work. On the other hand, the photochemical work of Maurizio Padoa is completely forgot. He worked with Ciamician until 1920 when he was designated as extra professor at the University of Cagliari, and then he was nominated full professor at the University of Parma. In 1924 he returned in Bologna to maintain the chair of Industrial Chemistry. He continued to study the photochemical properties of some organic and inorganic compounds. During Fascism he had some problems. First, he firmed the appeal of antifascist intellectuals promoted by Benedetto Croce. Then, he was suspended because his suspect on an assistant, a fascist assistant, and transferred to the University of Modena. In 1938, with the promulgation of race laws in Italy, being Padoa of Jewish religion, he was expelled from the University. In 1944 he was taken by fascist and nazist soldiers in his farm. He dead at Auschwitz.

Here we want to present an article he published on the *Gazzetta Chimica Italiana* in 1911, while it was an assistant of Ciamician. In this work we tested the possible use of circularly polarized light to induce a chiral reaction. He tested the reaction of angelic acid with bromine. The reaction mixture was completely different when the reaction was performed in the dark or in the presence of light.

The use of circularly polarized light did not give a chiral reaction. The result was in agreement with some other results obtained by for example by Cotton and can be explained on the basis of what we know on the mechanism of this reaction. For a discussion of CPL to induce a chiral reaction see Ref. 1.



Gazzetta Chimica Italiana **1911**, *41* (I), 469

Tentativo di sintesi asimmetrica con la luce polarizzata circolarmente

M. Padoa

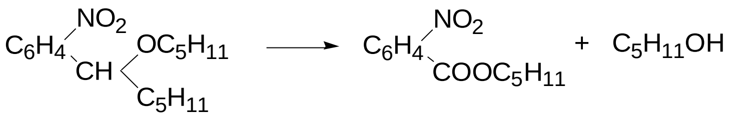
Il problema della origine naturale dei corpi otticamente attivi fu posto fin dai tempi di Pasteur. Questi pensava che per la formazione di un corpo otticamente attivo in una reazione, occorresse l'intervento di un'*azione di dissimmetria* che poteva essere anche fisica.

Le Bel e Van't Hoff suggerivano a tal uopo l'uso della luce polarizzata circolarmente fatta agire in modo da produrre corpi otticamente attivi.

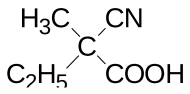
La luce polarizzata circolarmente appare infatti come uno dei mezzi più frequenti di cui possa valersi la natura; secondo A. Byk ([1]) essa, che si trova sempre commista alla luce ordinaria, deve certamente condurre al risultato desiderato. In questo senso fece dei tentativi Cotton ([2]), che dà anche un istruttivo resoconto dello stato attuale della questione.

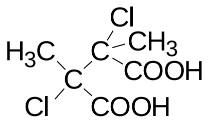
Il Cotton tentava di rendere attive soluzioni di racemato di rame facendovi agire la luce polarizzata circolarmente e pensando che l'uno dei due componenti otticamente attivi venisse distrutto più rapidamente dell'altro – e ciò in corrispondenza del diverso potere assorbente degli antipodi ottici rispetto alla luce polarizzata desta e sinistra. Queste esperienze ebbero risultato negativo.

Freundler ([3]) pensò di far agire la luce polarizzata circolarmente sull'acetale amilico *r* dell'aldeide o-nitrobenzoica. Si forma, secondo la reazione di Ciamician e Silber, l'etere amilico dell'acido o-nitrobenzoico e dell'alcool amilico.

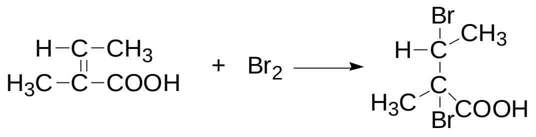


Ma nessuno dei due prodotti risultò otticamente attivo.
Henle e Haakh (4) partirono pure da due acidi contenenti atomi di carbonio asimmetrico:





Da questi, per azione della luce polarizzata circolarmente, eliminarono anidride carbonica utilizzando l'azione catalitica dei sali d'uranile. Ma non ottennero che corpi inattivi.
Io pensai che avrebbe avut maggiore probabilità di successo un tentativo fatto utilizzando una reazione nella quale avvenisse la formazione dell'atomo di carbonio asimmetrico. Come tale mi si presentò la bromurazione dell'acido angelico. Dico subito che però anche il mio tentativo si risolse negativamente.
Wislicenus (5) ha trovato che facendo agire il bromo sull'acido angelico, in modo che quest'ultimo si trovi sempre in eccesso, si hanno risultati completamente diversi, secondo che si agisce al buio o alla luce.



Nel primo caso si forma quasi totalmente del dibromuro dell'acido angelico; nel secondo caso quasi esclusivamente il corrispondente derivato dell'acido tiglico. Così, in esperienze a luce diffusa in ambiente ben rischiarato, Wislicenus ottenne 11,26% del primo e 87,74 del secondo.
La formazione del derivato tiglico è dunque una reazione che risponde al requisito di essere determinata dalla luce: in essa si formano due atomi di carbonio asimmetrico. La reazione inoltre è più rapida delle altre citate, poiché con buona illuminazione può essere

condotta a termine in un paio d'ore; ciò diminuisce i pericoli della racemizzazione dei corpi attivi eventualmente formati.

PARTE SPERIMENTALE

L'acido angelico che mi occorreva lo estrassi da un olio di camomilla romana fornito dalla casa Schimmel e C. di Miltitz.

Dopo averlo saponificato con potassa a lieve calore, separai l'acido angelico dal tiglico, che era presente, in parte col metodo di Fittig (6), basato sulla diversa solubilità dei sali di calcio dei due acidi, e in parte col metodo di Wislicenus (che consiste nel far congelare la miscela dei due acidi). Ottenni dell'acido angelico che si separò in grossi cristalli dall'etere di petrolio e fondeva esattamente a 45°, come indica Wislicenus.

Anzitutto eseguii una prova di bromurazione nelle condizioni indicate da Wislicenus per ottenere il bibromuro dell'acido tiglico. Gr. 0,04 di acido angelico sciolti in 2 ccm. di solfuro di carbonio vennero esposti alla luce solare, mantenendo fredda la soluzione con ghiaccio. Gr. 0,08 di bromo sciolti in 2 ccm. di solfuro di carbonio, vennero aggiunti gradualmente. A bromurazione terminata, la soluzione svaporata lasciò un corpo cristallino che fondeva a 75°. Il p.f. del bibromuro tiglico puro essendo 87,5°, si vede che la bromurazione aveva condotto, conforme ai dati di Wislicenus, ad una miscela di bibromuro dell'acido tiglico e di bibromuro dell'acido angelico, in cui il primo si trovava presente in quantità assai preponderante.

Verificai poi, esaminandone al polarimetro una soluzione al 10% in solfuro di carbonio, che l'acido angelico da me ottenuto non conteneva come impurità alcun corpo otticamente attivo.

Per eseguire l'esperienza di bromurazione alla luce polarizzata circolarmente, dovetti adottare una disposizione speciale, essendo necessario raffreddare con ghiaccio. La soluzione dell'acido angelico, gr. 0,35 in 5 ccm, di solfuro di carbonio, era contenuta in un piccolo palloncino; nel collo di questo passava un tubo proveniente da piccolo recipiente di vetro munito di robinetto, nel quale si trovava una soluzione di gr. 0,70 di bromo in 5 ccm. di solfuro di carbonio.

Il palloncino si trovava nell'interno di una scatoletta di legno; il tubo del recipiente superiore passava attraverso un tappo che intercettava completamente la luce; nel fianco della scatoletta, in faccia al palloncino, era praticato un foro, di fronte al quale era applicato un grosso nicol provvisto di una lamina di mica ¼ d'onda spostata di

45° in senso negativo rispetto alla diagonale minore del nicol. Tale disposizione permette di ottenere, per una data lunghezza d'onda, dei raggi polarizzati circolarmente, per le altre lunghezze d'onda raggi più o meno ellittici. Per raffreddare convenientemente la soluzione feci costruire una cassetta che ne conteneva un'altra sospesa nel suo interno; un largo tubo faceva comunicare la cassetta interna coll'esterno, ponendo in quest'ultima la scatoletta di legno sopradescritta, provvista di nicol. Il raffreddamento si otteneva riempiendo di ghiaccio e sale il vano fra le due cassette.

Dopo aver preparato tutto quanto e aver lasciato che il raffreddamento divenisse sufficiente si fece la bromurazione esponendo l'apparecchio alla luce solare. L'operazione ebbe la durata di ore 1 ½ circa. La soluzione venne subito svaporata per eliminare tracce di bromo non combinato; ridisciolto il prodotto in ccm. 7 circa di solfuro di carbonio, lo esaminai al polarimetro in un tubo lungo cm. 10. Ma entro i limiti degli errori d'osservazione, non potei osservare nessuna deviazione.

Cosicchè bisogna concludere che, anche in questo caso, la luce polarizzata circolarmente si manifesta inefficace allo scopo prefisso, oppure che la quantità di prodotto attivo formato è tanto minima da sfuggire all'osservazione, o ancora, che è avvenuta la racemizzazione.

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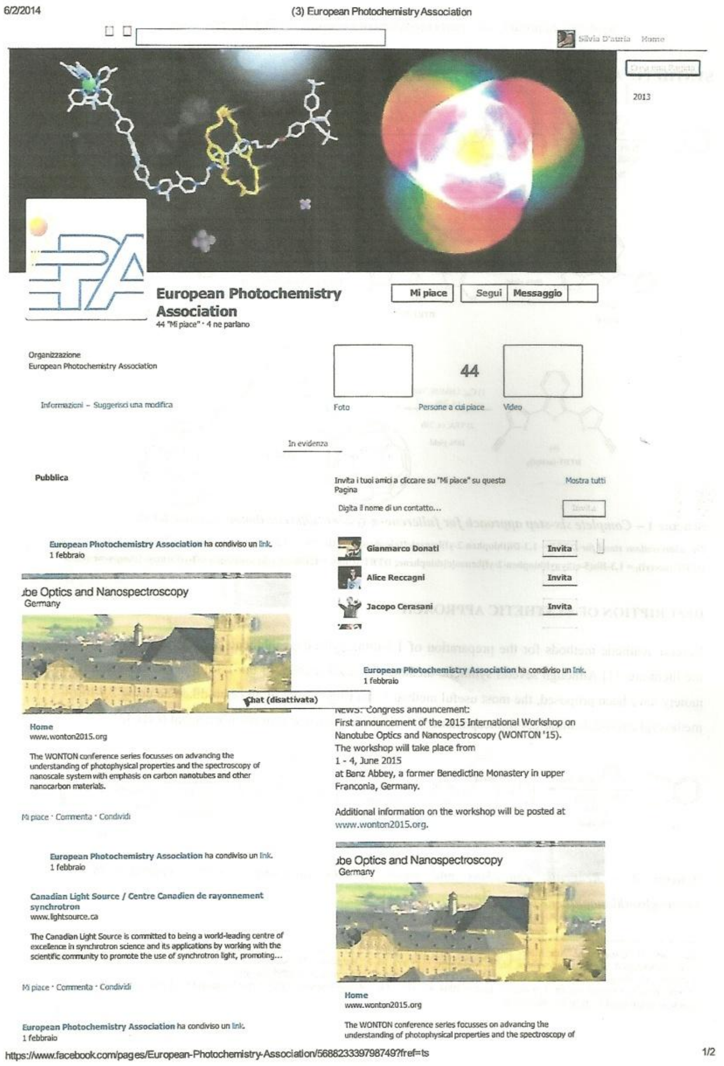

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NEWS: Congress announcement:
First announcement of the 2015 International Workshop on Nanotube Optics and Nanospectroscopy (WONTON '15).
The workshop will take place from
1 - 4, June 2015
at Banz Abbey, a former Benedictine Monastery in upper Franconia,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

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

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

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ABSTRACT OF THESIS ON PHOTOCHEMISTRY

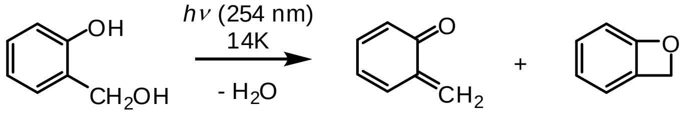
Synthesis, Photochemical Reaction Mechanisms of Formation, and Biological Activity of Benzene, Naphthalene and Anthracene Quinone Methides

Đani Škalamera
Department of Organic Chemistry and Biochemistry, Ruđer Bošković Institute, Zagreb, Croatia

Ph.D. Thesis (in Croatian), 2015; Research Adviser: Nikola Basarić

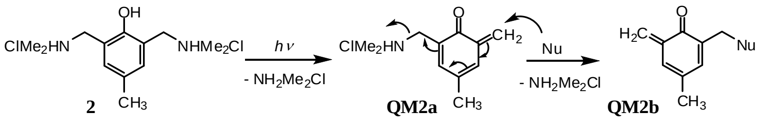
This Thesis comprises synthesis and investigation of photochemical reactivity of three series of quinone methide (QM) precursors, which are derivatives of benzene, naphthalene and anthracene. The photoreactivity of compounds has been studied in solid state at 14 K for 2-hydroxymethylphenol (**1**), and in solution at room temperature for Mannich derivatives of *p*-cresol, naphthalene and anthracene derivatives. Mechanisms of photochemical reactions were studied in solution by preparative irradiations, by UV-vis and fluorescence spectroscopy and by laser flash photolysis (LFP).

The photodehydratation of compound **1** in solid state at 14 K gave a mixture of *o*-QM and benzoxete, which were detected by IR spectroscopy.

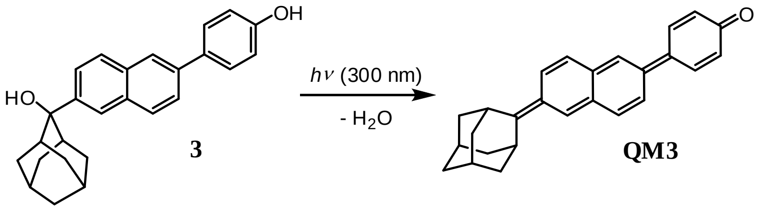


1 **QM1** **BO1**

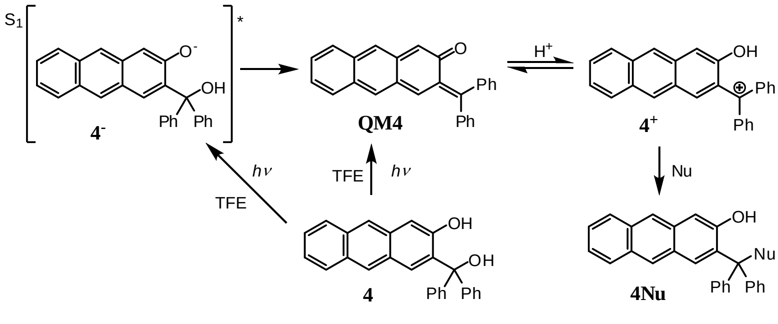
A mechanistic investigation of photodeamination in Mannich derivatives of *p*-cresol was conducted, demonstrating that the attack of nucleophiles to bifunctional **QM2a** generates new **QM2b**. This observation is of particular importance in the biological systems since it could be applied to DNA cross-linking.



Naphthalene derivatives were designed to investigate the optimal substitution pattern on the naphthalene chromophore for the most efficient photodehydratation. Derivative **3** underwent the most efficient photodehydration to QM3, indicating that a 2,6-substitution is optimal.



Photogeneration of QMs from anthracenes is interesting because of potential application in biology, given that the chromophore absorbs at wavelengths >400 nm. Anthracene derivatives were prepared by a multistep synthetic procedure starting from 2-aminoanthraquinone. Formation of reactive intermediates from **4** was probed by LFP wherein **QM4** was detected. It was shown that **QM4** undergoes protonation to give the cation that subsequently reacts with nucleophiles.



Antiproliferative investigation on human cancer cell lines was conducted on several series of compounds with and without exposure to irradiation. 3-Hydroxymethyl-2-anthrol (**5**) was found as a *lead molecule* which is not toxic without irradiation (IC_{50} > 100 mM), whereas irradiation significantly increased the antiproliferative activity (for HCT 116, human colon cancer cell line, IC_{50} is 1 ± 0.4 mM after 3×15 min of irradiation on 420 nm). The observed enhancement of antiproliferative activity upon irradiation can be correlated to the photochemical generation of reactive QMs.

Publication:
"Photosolvolysis of bulky (4-hydroxyphenyl)naphthalene derivatives" Đ. Škalamera, K. Mlinarić-Majerski, L. Uzelac, M. Kralj, P. Wan, N. Basarić, Photochem. Photobiol. Sci. 2013, 12, 2043-2056.
"Near-visible light generation of a quinone methide from 3-hydroxymethyl-2-anthrol" Đ. Škalamera, K. Mlinarić-Majerski, I. Martin-Kleiner, M. Kralj, P. Wan, N. Basarić, J. Org. Chem. 2014, 79, 4390-4397.

ANNOUNCEMENTS

CECP 2016 Conference Invitation

Stephan Landgraf
Institute PTC, Graz University of Technology, 8010 Graz, Austria

From Sunday, February 14 to Thursday, February 18, 2016, photochemists from different countries will come together to share their results and experiences at the Congress Centre of Bad Hofgastein/Austria.
The scientific organization has been done by the international scientific committee: Michael **Tausch**, Wuppertal, D; Andrzej **Sobolewski**, Warsaw, PL, Petr **Klán**, Brno, CZ; Alexandre **Fürstenberg**, Geneva, CH, Sylvie **Lacombe**, Pau, F; Alberto **Credi**, Bologna, I. The conference will start on Sunday with the EPA come together including a buffet and an opening lecture.
6 plenary lectures are planned: Jacek **Waluk**, Warsaw, PL, "Various ways of looking at single molecules", Stefan **Hecht**, Berlin, D, "Designing photoswitches with improved performance", Natalie **Banerji**, Fribourg, CH, "Spectroscopic Investigations of Organic Electronic Materials", Paola **Ceroni**, Bologna, I, "Light-harvesting antennae based on luminescent silicon nanocrystals", Petr **Slavicek**, Praque, CZ, "Computational Photodynamics: From UV to X-ray domain", and Suzanne **Fery-Forgues**, Toulouse, F, "The Tao of solid-state fluorescent organic molecules: On the Way to luminescent microfibres and nanoparticles for biomedical imaging"
Deadlines are: Submission of short talk applications: December 1, 2015. Submission of poster applications: January 1, 2016. Registration: January 1, 2016, and travel grant applications: January 1, 2016.
Official web site of the meeting is www.cecp.at

26th IUPAC International Symposium on Photochemistry

Dear Colleague,

It is my great pleasure to inform you that XXVIth IUPAC Symposium on Photochemistry (2016 IUPAC Photochem) at Osaka City Central Public Hall, Osaka, Japan, on April 3 -8, 2016.On behalf of the organizing committee, we are delighted to inviteou to this Symposium. I am sure that your participation and haring of recent achievements would be a precious opportunity for the society members.

Date: April 3-8, 2016
Venue:Osaka City Central Publich Hall, Osaka, Japan

Please kindly visit our offical symposium website (http://we.apollon.nta.co.jp/iupac2016) for further information about 2016 IUPAC Photochem..

Please note that this invitation includes no offer of financial support.

I would be very pleased and honored if you could accept this invitation.
we are looking forward to a favorable reply from you soon.

Sincerey yours,

Tetsuro Majima
Chairperson, XXVIt Iupac Symposium on Photochemistry (2016 IUPAC Photochem) at Osaka City Central Public Hall, Oska, Japan, on April 3 - 8, 2016.

Secretariat for the 26th IUPAC
c/o West Japan MICE Sales Division, Nippon Travel Agency Co. LTD.
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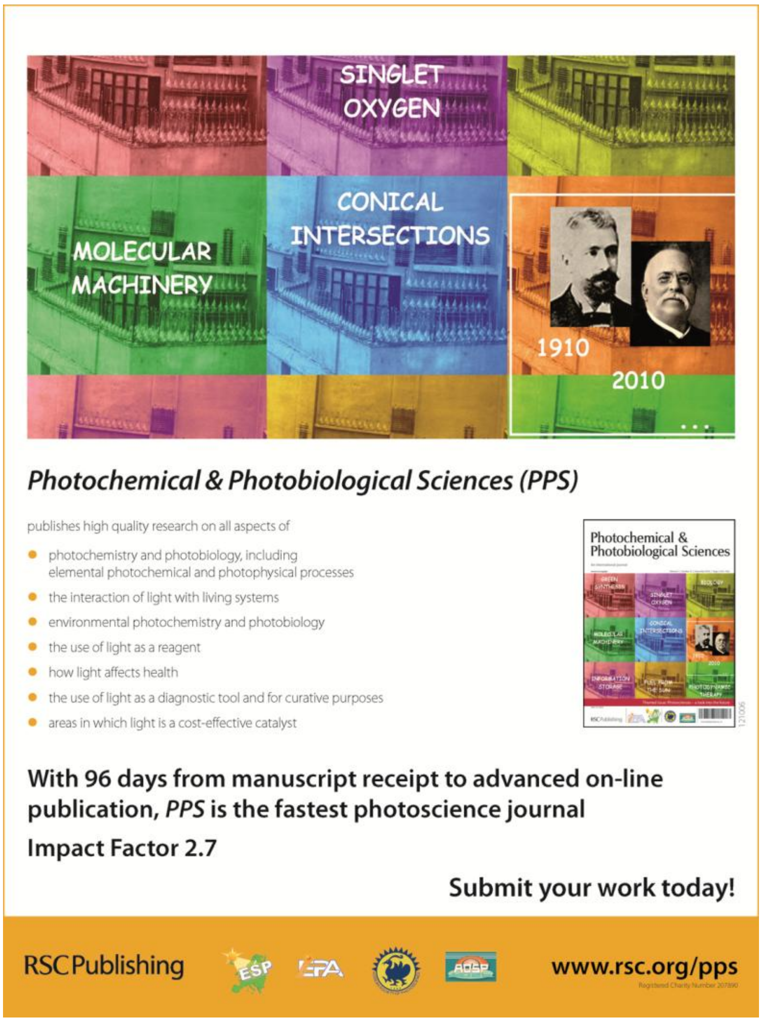
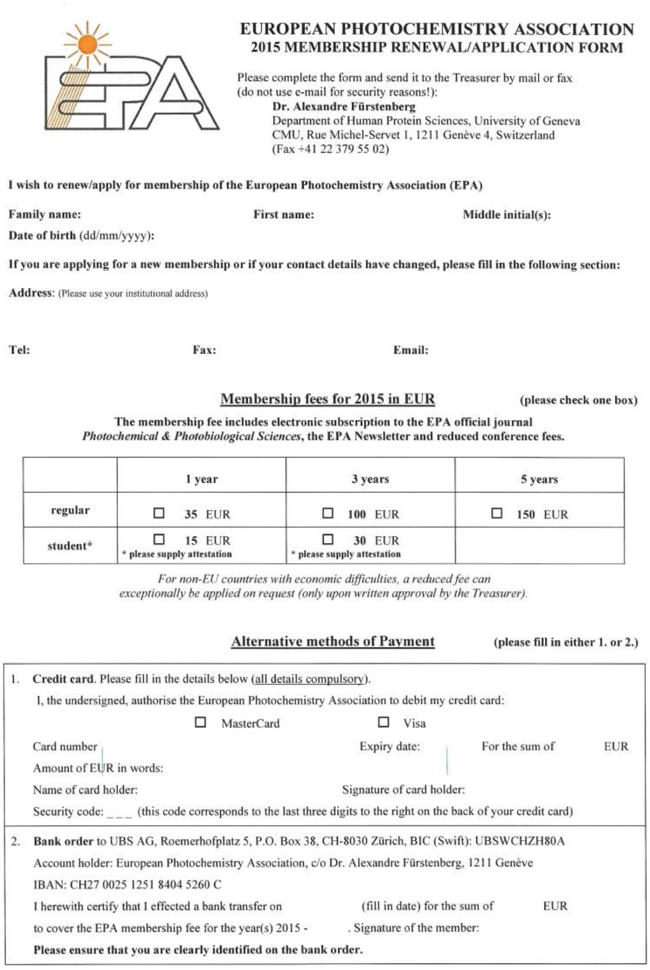
PHOTOCHEMICAL AND PHOTOBIOLOGICAL SCIENCES



MEMBERSHIP APPLICATION FORM



EUROPEAN PHOTOCHEMISTRY ASSOCIATION
2015 MEMBERSHIP RENEWAL/APPLICATION FORM

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

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

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

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European Photochemistry Association

NEWSLETTER

No. 90, June 2016

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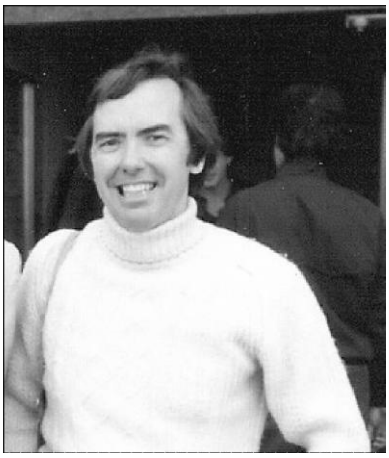
EDITORIAL

President's Letter

Dear Colleagues,

In this, my final newsletter as President before handing over to Julia Perez, I'll start in usual fashion; my weather update. I'm writing this on the occasion of the Summer Solstice (a day earlier than usual due to it being a leap year), where we have the longest number of hours of daylight of any day of the year – so should be perfect for photochemistry! However Loughborough is grey and wet; summer seems to have been and gone.
A couple of weeks ago saw the 80th birthday of Frank Wilkinson, Professor of Physical Chemistry at Loughborough University from 1982 to his retirement in 2001. Many members will know him as a friend and collaborator, and also as Secretary of the EPA from 1980-1984, Chairman from 1984-1988, and Chair of the Scientific committee of the XI IUPAC Symposium on Photochemistry in Lisbon in 1986. He was also one of the Founding Editors-in-Chief of PPS from 2001 to 2006. His retirement symposium at Loughborough University in 2001 was attended by many members. Happy Birthday Frank!



2016 saw the awarding of three prizes in the area of photochemistry, recognising both outstanding contributions and outstanding potential.

These included the *EPA-PPS Prize* for the most highly cited paper published in PPS during the previous two calendar years, and the *EPA Prize for Best PhD Thesis in Photochemistry* published during the previous two calendar years, which were presented at the CECP in Bad Hofgastein in February this year to Fausto Ortica and Tomáš Slanina, respectively.

The *Porter Medal*, in cooperation with our Inter-American and Asian/Oceanian photochemistry association counterparts, I-APS and APA, has been awarded jointly to two nominees; Prof. James Barber and Prof. Fred Lewis. Both I'm sure you will agree are worthy winners. The medals themselves will be presented later in the year during the Asian and Oceanian Photochemistry Conference in Singapore.

Almost finally, a reminder about our Facebook page; please "like" us to keep up-to-date with conferences, job opportunities and general news.

And finally thanks are due to Werner Nau and John Gilchrist for their contributions to the committee and who are stepping down from the committee this Summer.

Dr. David Worrall
Loughborough University

PUBLICATIONS

THE HISTORY OF THE IUPAC SYMPOSIA ON PHOTOCHEMISTRY – A SUCCESS STORY [1]

Silvia E. Braslavsky
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The Symposia were started by the initiative of *George S. Hammond* (1921-2005) (Figure 1) in Strasbourg in 1964, a banner year for Photochemistry since it was the same year the first Gordon Conference on Photochemistry took place [2].

Figure 1. George Hammond (1921-2005)
(from: http://web.pdx.edu/~wamserc/Hammond/)

This historical review is intended to help us remember the persons who shaped the Symposia as well as to survey the main subjects treated over the years as I see them using my personal, certainly biased, glasses. Of great help for the writing of this paper have been the publication by Ugo Mazzucato about the history of the

European Photochemical Association (EPA) [3] and the reports written by many colleagues and published after each Symposium (with some exceptions) in the EPA Newsletters, after 1978.

In 1964 the meeting, already supported by IUPAC, was called the International Symposium on Organic Photochemistry and in size and style was reminiscent of a Gordon Conference. *W. Albert Noyes Jr.* (1898-1980) who was at the time the President of IUPAC, gave a talk on "Some aspects of transitions between electronic levels"; it was published together with *I. Junger* in *Pure and Applied Chemistry* [4]. Since 1967 the Symposium has been called the "IUPAC Symposium on Photochemistry" and is regularly held in even years usually at the end of July [5]. The Symposium was held outside Europe in 2006 in Kyoto, Japan [see Table 1 for the list of sites, chairmen (one a chairwoman) and local organizers] and is planned to be again in Japan in 2016. The Japanese photochemical community has been very productive and creative and it has strongly collaborated to finance the Symposia. As a result, the number of Japanese participants has significantly increased over the years. Since 1964 also quite generally the number of participants and countries represented have grown substantially, and the subjects discussed have incorporated all areas of research in which light is used, be it photophysics and its instrumentation, micro- and nanoscopies, photochemistry, photobiology, the molecular basis of photomedicine, material sciences, solar energy conversion, photocatalysis, analytical chemistry, and so forth.

The photochemists more interested in the photophysical aspects and instrumentation already had two other series of meetings running: (1) One that later became the International Conference on Photochemistry (ICP), which started in 1962 [6] and (2) the Informal Conference on Photochemistry, initiated in 1952 by *Francis E. Blacet* (1899-1990) and held in North America every two years [7] until 2000 in San Juan, Puerto Rico [8].

The Chairperson of each IUPAC Symposium selects the Scientific Chairperson of the IUPAC Symposium to be held four years later, after adequate consultation. The selected Chairperson chooses a scientific Committee, the location and local organizer, requests the sponsorship by IUPAC (in general a patronage with no financing) and is responsible for the scientific standard and quality control of the Symposium.

Table 1: List of IUPAC Symposia on Photochemistry

Year	**Symposium Number**	**Site**	**Scientific Chairperson**	**Chair of Local Organizing Committee**
1964	Organic Photochemistry, Part of a NATO series	Strasbourg, France	G. S. Hammond, USA	J. Levisalles
1967	II	Enschede, The Netherlands	W. G. Dauben, USA	E. Havinga and M. Kronenberg
1970	III	St Moritz, Switzerland	D. Bryce-Smith, UK	K. Schaffner
1972	IV	Baden-Baden, Germany	H. E. Zimmerman, USA	D. Döpp
1974	V	Enschede, The Netherlands	O. L. Chapman, USA	J. J. C. Mulder
1976	VI	Aix-en-Provence, France	K. Schaffner, Switzerland	J. Kossanyi and M. Julliard
1978	VII	Leuven, Belgium	N. J. Turro, USA	F. de Schryver
1980	VIII	Seefeld, Austria	H. Dürr, Germany	J. G. Schantl
1982	IX	Pau, France	J. Joussot-Dubien, France	E. Poquet and H. Bouas-Laurent
1984	X	Interlaken, Switzerland	D. J. Whitten, USA	A. M. Braun
1986	XI	Lisbon, Portugal	F. Wilkinson, UK	S. M. B. Costa

1988	XII	Bologna, Italy	V. Balzani, Italy	F. Bolletta
1990	XIII	Warwick, UK	F. D. Lewis, USA	R. S. Davidson
1992	XIV	Leuven, Belgium	F. De Schryver, Belgium	D. De Keukeleire
1994	XV	Prague, Czech Republic	J. Michl, USA	I. Stibor
1996	XVI	Helsinki, Finland	J. Wirz, Switzerland	H. Lemmetyinen
1998	XVII	Sitges, Spain	R. A. Caldwell, USA	J. Font
2000	XVIII	Dresden, Germany	S. E. Braslavsky, Germany	T. Wolff
2002	XIX	Budapest, Hungary	H. D. Roth, USA	J. Nyitrai
2004	XX	Granada, Spain	M. A. Miranda, Spain	B. Quintero
2006	XXI	Kyoto, Japan	M. Irie, Japan	A. Osuka
2008	XXII	Gothenburg, Sweden	D. Gust, USA	B. Albinsson
2010	XXIII	Ferrara, Italy	F. Scandola, Italy	C. Chiorboli
2012	XXIV	Coimbra, Portugal	H. D. Burrows, Portugal	A. J. M. Valente
2014	XXV	Bordeaux, France	D. M. Bassani, France	A. del Guerzo and N. McClenaghan
2016	XXVI	Osaka, Japan	T. Majima, Japan	

Although the Symposia have all been held in Europe (with the exceptions mentioned above, i.e., in 2006 in Kyoto and the next one in 2016 in Japan), 10 of the first 20 Scientific Chairmen were from the USA, alternating with those from European Countries (see Table 1; the local organizer was always a photochemist at or near the site of the Symposium). The more recent change in this practice reflects both declining USA participation, mainly due to the reduced support by the USA funding agencies, as well as a simplified logistics when the Scientific Chairperson lives near the conference site.

During each Symposium, as well as during the International Conference on Photochemistry, there is usually a regular meeting of the Sub-Committee of Photochemistry (formerly the Commission on Photochemistry) of IUPAC to discuss ongoing projects and consider new ones, as well as to choose new members of the Sub-Committee.

A very well attended exhibition of instruments has been organized at most of the Symposia and, needless to say, an impressive number of posters has been presented each time by very talented young and not-so-young colleagues active in the field.

EPA holds its biannual assembly on one of the evenings during the week of the Symposium. This is one of several reasons to hold the Symposium in Europe. In short, the other reasons are (i) the Gordon Conference on Photochemistry is held in North America every two years, (ii) the American photochemists (Inter-American Photochemical Society, I-APS) hold their annual meeting every start of the year (usually January 1 – 4) in Florida and once every five years in Latin America, so far four times, namely 1996 in Foz de Iguazú (Brazil), 2001 in Ascochinga (Argentina), 2006 in Salvador de Bahia (Brazil), and 2011 in Mendoza (Argentina), [evidently, the American photochemical community has sufficient opportunities to meet near home], (iii) the Asian and Oceania Photochemical Association meets annually in their own area, (iv) there is so far no other pan-European Conference on Photochemistry, and (v) the "other" Photochemistry Congress (ICP) travels the world, the last one was held in Leuven in 2013 and the next one is scheduled for Jeju Island, Korea, in 2015.

The titles of the contributions to the first Symposium in 1964 show a strong interest in photochemical studies of carbonyl-containing molecules, and some interest in compounds with conjugated double bonds. The titles and authors of the papers published in *Pure and Applied Chemistry* (*PAC*), the Scientific Journal of IUPAC [1,4], are listed in Table 2. All plenary lectures and some invited lectures after the initial Symposia were published in *PAC*. Later on, due to several reasons, not all of the lectures were published in *PAC*. I have included in this presentation the complete list of papers published in *PAC*, as it is found in the webpage of IUPAC, for each Symposium. For the sake of consistency, I am including the initials of the names of the authors, although in the *PAC* indexes, the authors are sometimes listed with full names and other times with initials.

Table 2. First IUPAC Symposium on Photochemistry – Strasbourg – France, 1964. A selection of the titles published in [4].[1]

W. A. Noyes, Jr. and I. Unger, Some aspects of transitions between electronic levels
E. J. Bowen, Chemiluminescence in solution
M. Mousseron, Isomérisation photochimique de systèmes polyéniques
H. E. Zimmerman, Report on recent photochemical investigations
G. Porter and P. Suppan, Reactivity of excited states of aromatic ketones
K. Gollnick and G. O. Schenck, Mechanism and stereoselectivity of photosensitized oxygen transfer reactions
H. M. Frey, Photolysis of the diazirines
W. G. Dauben and W. T. Wipke, Photochemistry of dienes
O. Jeger, K. Schaffner and H. Wehrli, Photochemical transformation of α,α-epoxyketones and related carbonyl systems
M. D. Cohen, Photochemistry of the organic solid state
R. C. Cookson, Stereospecificity in photochemical reactions of ketones
O. L. Chapman, Photochemistry of unsaturated nitrocompounds
N. C. Yang, Photochemical reactions of carbonyl compounds in solution: Paterno-Büchi reaction
P. de Mayo, Photochemical reactions of dicarbonyl compounds
G. Quinkert, Photochemistry of non-conjugated ketones in solution

The second Symposium in Enschede was chaired by William G. Dauben (1919-1997) (Figure 2), and organized by M. E. Kronenberg and Egbert Havinga (1909-1988) (Figure 3).

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[1] The name of the presenter has been underlined. In few cases I could not identify the speaker.

Figure 2. William (Bill) G. Dauben (1919 -1997)
From Guest Book, Max Planck Institute for Radiation Chemistry

Figure 3. Egbert Havinga (1909-1988)
From http://www.kncv.nl/chemie-historische-groep-%28chg%29/geschiedenis-van-de-chemie/h-biografieen-nederlandse-chemici.117066.lynkx

Table 3. IInd IUPAC Symposium on Photochemistry – Enschede – The Netherlands, 1967. Titles of the papers published in [5]

D. H. R. Barton, The use of photochemical reactions in organic synthesis
H. Prinzbach, Photochemical reactions with non-conjugated dienes
D. Bryce-Smith, Photoaddition and photoisomerization reactions of the benzene ring
R. Srinivasan, Mercury (${}^3P_1$) sensitized photoreactions of furan: Details of the primary processes
K. Schaffner, Cyclic ketones: Photolytic eliminations and reductions
S. Sato, Photosensitized isomerizations of dideuteroethylenes
P. Yates, Photochemistry of cyclic ketones in solution
A. Weller, Electron-transfer and complex formation in the excited state
L. M. Stephenson and G. S. Hammond, Fate of the excitation energy in the quenching of fluorescence by conjugated dienes
E. Havinga and M. E. Kronenberg, Some problems in aromatic photosubstitution
E. Müller, Mechanism of the Tübingen photooximation reaction
J. Rigaudy, Photooxydation des dérivés aromatiques
P. D. Bartlett, R. Helgeson and O. A. Wersel, Singlet and triplet states in cycloaddition to conjugated dienes

Figure 4. Derek Bryce-Smith (1926-2011)
From: The Guardian, July 19th 2011.

Table 3 shows the titles of the published contributions arising from that symposium. The lecture by Albert Weller (1922-1990) on "Electron-transfer and complex formation in the excited state", presented a then novel aspect which later became fundamental to our understanding of many photoinduced reactions. In the excellent book "Photochemistry" authored by Jack G. Calvert and James N. Pitts Jr. (1921-2014) (Wiley, 1966) there is no mention yet of any electron transfer processes or of the existence of ion radicals. Shin Sato from Tokyo University presented excited-mercury photosensitization [excitation by (3P1) Hg, then a frequently used technique in the gas phase] for photosensitized isomerizations, and searched for other photosensitizers (e.g., benzene).

The third Symposium in 1970 in Saint Moritz was chaired by Derek Bryce-Smith (1926-2011) (Figure 4) and locally organized by Kurt Schaffner (Figure 5).

Figure 5. Kurt Schaffner
Private photo collection (SEB)

Table 4. IIIrd IUPAC Symposium on Photochemistry – St Moritz – Switzerland, 1970. All Plenary Lectures were published in [9].

T. Förster, Diabatic and adiabatic processes in photochemistry
A. W. Adamson, Recent advances in the photochemistry of coordination compounds
M. A. El-Sayed, Multiple resonance techniques in the study of the magnetic, radiative and non-radiative properties of the triplet state
H. Labhart, W. Heinzelmann and J. P. Dubois, On the search for the mechanism of photoreactions of some heterocyclic compounds
J. Meinwald, J. W. Young, E. J. Walsh and A. Courtin, Photochemical transformations of divinyl arenes
D. R. Arnold, A. B. Evnin and L. A. Karnischky, The electronic excited states of small ring compounds: heterobicyclopentanes
T. Bercovici, R. Korenstein, K. A. Muszkat and E. Fischer, Dianthrone photochromism 1950-1970
R. Hoffmann, Geometry changes in excited states
P. J. Kropp, Photochemistry of alkenes in solution
A. A. Lamola, Triplet photosensitization and the photobiology of thymine dimers in DNA
F. McCapra, The chemiluminescence of organic compounds

Triplet photosensitization (*Angelo A. Lamola*) was a relatively novel subject at that moment (only twelve papers were in the literature until 1970) and certainly the field had an impressive development afterwards. The contribution by *Theodor Förster* (1910-1974) reflects the effort to classify the photochemical reactions based on the moment of transition between potential energy surfaces of ground state reactants through excited-state surfaces to ground-state products. *Jakob Wirz* (who was present at that Symposium) says that the young *Josef Michl* presented an impressive talk on the mechanism of the photochemical formation of pleiadene (see below). There was also a well-attended evening workshop on biradicals in which *Roald Hoffmann* and *Josef Michl* were active participants. Years later, when *Josef Michl* was a member of the IUPAC Commision on Photochemistry and we (I was also a member of that Commission) elaborated the first version of the Glossary of Terms used in Photochemistry [10], he took enormous care to ask a large number of photochemists about the biradical definition.

Howard Zimmerman (1926-2012) (Figure 6) chaired the fourth Symposium in 1972 and brought it to Baden-Baden in Germany with the local organization in charge of his former post-doctoral collaborator *Dietrich Döpp* and his wife *Heinrike Döpp* (Figure 7)

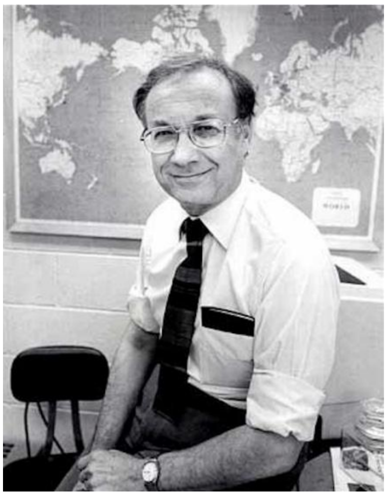

Figure 6. Howard Zimmerman (1926-2012)
From: Wikipedia

Figure 7. Heinrike and Dietrich Döpp in Baden – Baden.
From: Dietrich Döpp private collection

Table 5. IVth IUPAC Symposium on Photochemistry – Baden-Baden – Germany, 1972. Selected titles of the papers published in [11].

J. A. Barltrop, The photoreduction of aromatic systems

W. G. Dauben, M. S. Kellogg, J. I. Seeman, N. D. Vietmeyer and P. H. Wendschuh, Steric aspects of the photochemistry of conjugated dienes and trienes

K. Gollnick and H.-U. Stracke, Direct and sensitized photolysis of dimethyl sulphoxide in solution

H. Hart, The photochemistry of cycloheptadienones

A. Padwa, M. Dharan, J. Smolanoff and S. I. Wetmore, Jr, Recent advances in the photochemistry of the carbon-nitrogen double bond

G. Quinkert, Photochemistry of linearly conjugated cyclohexadienones in solution

L. Salem, Diradicals

K. Schaffner, Recent results on some photochemical rearrangements

P. Claus, T. Doppler, N. Gakis, M. Georgarakis, H. Giezendanner, P. Gilgen, H. Heimgartner, B. Jackson, M. Märky, N. S. Narasimhan, H. J. Rosenkranz, A. Wunderli, H.-J. Hansen and H. Schmid, Photochemistry of some heterocyclic systems

N. (Nick) J. Turro and P. Lechtken, Thermal and photochemical generation of electronically excited organic molecules. Tetramethyl-1,2-dioxetane and naphthvalene

A. Zweig, Photochemical generation of stable fluorescent compounds (photofluorescence)

Figure 8. Orville L. Chapman (1932 - 2004)
From
http://www.chem.ucla.edu/dept/Organic/OLC_Brochure.html

Table 6. Vth IUPAC Symposium on Photochemistry – Enschede – The Netherlands, 1974. Papers published in [12].

J. Cornelisse, Photosubstitution reactions of aromatic compounds
A. Devaquet, Avoided crossings in photochemistry
B. Blank, A. Henne, G. P. Laroff and H. Fischer, Enol intermediates in photoreduction and type I cleavage reactions of aliphatic aldehydes and ketones
C. S. Foote and T. R. Darling, Decomposition of dioxetanes: a unique probe into mechanism and energy transfer processes
J. Michl, Model calculations of photochemical reactivity
M. Pape, Industrial applications of photochemistry
J. Saltiel, D. W. L. Chang, E. D. Megarity, A. D. Rousseau, P. T. Shannon, B. Thomas and A. K. Uriarte, The triplet state in stilbene *cis-trans* photoisomerization
H.-D. Scharf, H. Leismann, W. Erb, H. W. Gaidetzka and J. Aretz, The photocycloaddition of dichlorovinylene carbonate to benzene and naphthalene
D. I. Schuster, Energy wastage processes in ketone photochemistry
W. R. Ware, Photophysics of exciplexes: some kinetic aspects
F. Wilkinson, Quenching of triplet states of organic compounds by coordination complexes
M. S. Wrighton, D. S. Ginley, M. A. Schroeder and *D. L. Morse*, Generation of catalysts by photolysis of transition metal complexes

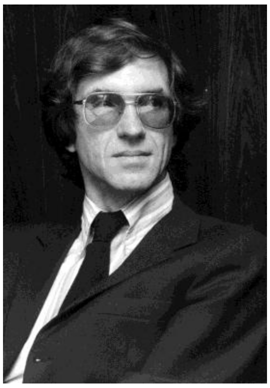

Figure 9. Chris Foote (1935 – 2005)
From Guest Book, Max Planck Institute for Radiation Chemistry

Nick Turro's (1938-2012) lecture on dioxetane and naphthvalene reflected the large influence of his group's research in the development of photochemistry. The papers on the thermal generation of excited molecules have received a very large number of citations.

In 1974 the Symposium returned to Enschede in The Netherlands and was chaired by Orville L. Chapman (1932-2004) (Figure 8) and locally organized by J. J. C. Mulder.

The calculations of trajectories of excited molecules started gaining importance (Devaquet and Michl). Very timely was the analysis of the photophysics of exciplexes by time-resolved and steady state fluorescence techniques presented by W. Ware. I would like to pay a tribute to Chris Foote (1935-2005) (Figure 9) and his contributions.

Figure 10. Jean Kossanyi (1933 – 2004)
From
http://pubs.rsc.org/En/content/articlelanding/2003/pp/b301834m/unauth#!divAbstract

In 1976 the Symposium was held in Aix-en-Provence, France; the Scientific Chair was *Kurt Schaffner* (see Figure 5) and the organizer *Jean Kossanyi* (1933-2004) (Figure 10).

Table 7. VIth IUPAC Symposium on Photochemistry – Aix-en-Provence – France, 1976. Titles of the papers published in [13].

N. C. Baird, What can photochemists expect from *ab initio* calculations now and in the near future?
F. C. De Schryver, N. Boens, J. Huybrechts, J. Daemen and M. De Brackelaire, Photochemistry of bichromophoric compounds: scope and expectations
J. E. Guillet, Studies of energy transfer and molecular mobility in polymer photochemistry
P. J. Wagner, Misleading sigmas and neglected geometries: the effects of methyl substitution on rates of triplet state hydrogen abstraction by the benzoyl group
J. J. Turner, J. K. Burdett, R. N. Perutz and M. Poliakoff, Matrix photochemistry of metal carbonyls
T. Mukai, T. Kumagai and O. Seshimoto, Photochemical and thermal reactions of some heterocycles containing C=N-O or N=C-O group
J. Streith, The photochemistry of aromatic-*N*-ylides. Rearrangement and fragmentation patterns
P. Courtot, R. Rumin and J.-Y. Salaun, Photochemistry of polyenes. Control by orbital symmetry and ground state conformations?
K. Nakanishi, Photochemical studies of visual pigments
T. Rosenfeld, B. Honig, M. Ottolenghi, J. Hurley and T. G. Ebrey, *Cis-trans* isomerization in the photochemistry of vision
H. D. Hartzler, Aromatic aldehyde-leuco dye photoxidation
P. B. Gilman, Jr., A review of the electrochemical boundaries for the photochemistry of spectrally sensitized silver halide emulsions
D. G. Whitten, F. R. Hopf, F. H. Quina, G. Sprintschnik, H. W. Sprintschnik, Photochemistry of organic chromophores incorporated into fatty acid monolayers
H. E. Zimmerman, Recent mechanistic and exploratory organic photochemistry

The first of the many reports to the IUPAC Symposia by Frans De Schryver's group on the work with multichromophoric systems was offered on this occasion, as well as two talks related to the photoisomerization of visual pigments, i.e., the retinal-containing proteins. An interesting lecture by Colin Baird was intended to convince the photochemists already in 1976 of the possibilities of ab initio calculations of the energetics of excited states. Koji Nakanishi entertained the guests at the banquet with some of his magic tricks.

Figure 11. Nick Turro (1938 – 2012)
From
http://www.columbia.edu/cu/news/02/05/nicholasTurro_nsf.html

The seventh Symposium was chaired by *Nicholas (Nick) Turro* (1938-2012) (Figure 11) and organized by *Frans De Schryver* (Figure 12) in 1978 in Leuven, Belgium. This was the first IUPAC Photochemistry Symposium I attended.

The first of numerous contributions of the Bologna group (*Balzani et al.*) to the IUPAC Photochemistry Symposia was presented as well as another one from the productive Bordeaux group [*Jacques Joussot-Dubien* (1928-2009) *et al.*]. A special workshop on the properties of biradicals was organized by *Peter Wagner* (1939-2009) and another one on new techniques was also held (see report of the Symposium in *EPA Newsletter*, [15]). Studies with monolayers such as, *e.g.*, Langmuir-Blodgett films, attracted considerable attention. This Symposium generated the firts report of an IUPAC Symposium on Photochemistry in the *EPA Newsletter*. The Newsletters themselves started to be published on a regular basis in January 1978 (see [3]). From that date on, there was almost always a report of the Symposium in the *EPA Newsletter*.

Figure 12. Frans De Schryver
From: EPA Newsletters, **62**, p. 23

Table 8. VIIth IUPAC Symposium on Photochemistry – Leuven – Belgium, 1978. Titles from the papers published in [14].

N. C. Yang, R. L. Yates, J. Masnovi, D. M. Shold and W. Chiang, Chemistry of exciplexes. Photocycloadditions of anthracenes to conjugated polyenes
J. Kossanyi, Photochemical approach to the synthesis of natural products
N. D. Epiotis, Thermal chemistry as an exercise in photochemistry!
G. Geuskens and C. David, The photo-oxidation of polymers. A comparison with low molecular weight compounds
S. Farid, P. A. Martic, R. C. Daly, D. R. Thompson, D. P. Specht, S. E. Hartman and J. L. R. Williams, Selected aspects of photochemistry in polymer media
A. M. Trozzolo, T. M. Leslie, A. S. Sarpotdar, R. D. Small, G. J. Ferraudi, T. D. Minh and R. L. Hartless, Photochemistry of some three-membered heterocycles
J. Joussot-Dubien, R. Bonneau, P. Fornier de Violet, R. Koussini, R. Lapouyade, Comparative kinetic study of the reactivity of molecules in their excited singlet and triplet states in the cases of an electron abstraction and an intramolecular photocyclization reaction
D. Schulte-Frohlinde and H. Görner, *Cis-trans* photoisomerization of 4-nitrostilbenes

V. Balzani, F. Bolletta, F. Scandola and R. Ballardini, Excited state electron-transfer reactions of transition metal complexes
O. L. Chapman, Photochemistry of diazocompounds and azides in argon
H. Kuhn, Electron transfer in monolayer assemblies

Heinz Dürr (Figure 13) chaired the eigth Symposium in 1980 in Seefeld; the local organizer was *J. G. Schantl* (Innsbruck).

Figure 13. Heinz Dürr
From: Guest Book, Max Planck Institute for Radiation Chemistry

Electron transfer and radical ions were prominently represented (*D. Arnold et al.*, *N. Sutin* and *C. Creutz*), the Bordeaux organic photochemistry group reported results its with photochromic materials (*H. Bouas-Laurent et al.,*), *Waldemar Adam* offered one of his very attractive lectures on the thermal generation of excited states, solar energy conversion started seriously engaging the scientists in a very multidisciplinary manner (*H. Gerischer*, 1919-1994), and the first plenary lecture on picosecond spectroscopy in a Photochemistry Symposium was offered by *Robin Hochstrasser* (1931-2013). *Günther Ohloff* (1924-2005) of Firmenich S.A. described the use of molecular singlet oxygen in organic synthesis for the industrial production of chemicals. The Japanese colleagues (*T. Matsuura et al.*) impressed the audience with their extraordinary creativity and productivity. Three

Workshops were organized: one on “New Techniques” by *Kurt Schaffner*, one on “Magnetic Fields in Photochemistry” by *Albert Weller* (1922-1996) and another one on “Photoimaging” by *Ed Chandross* (Bell Labs) with the participation of *Irena Bronstein-Bonte* from Polaroid Corporation, *G. Delzenne* from Agfa-Gaevert, *Samir Farid* from Kodak, and *H. Hartzler* from Dupont. This was an impressive industrial participation! See *EPA Newsletter* for a report of the Symposium [17].

Table 9. VIIIth IUPAC Symposium on Photochemistry – Seefeld – Austria, 1980. Papers published in [16].

W. Adam, Thermal generation of electronic excitation with hyperenergetic molecules
D. R. Arnold, P. C. Wong, A. J. Maroulis and T. S. Cameron, Radical ions in photochemistry. 12. The photoaddition of olefins to cyano aromatic compounds in polar solvents
P. S. Engel and C. J. Nalepa, Photochemical decomposition and isomerization of aliphatic azo compounds
H. Bouas-Laurent, Alain Castellan and J.-P. Desvergne, From anthracene photodimerization to jaw photochromic materials and photocrowns
H. Gerischer, Heterogeneous electrochemical systems or solar energy conversion
A. Gilbert, The inter- and intramolecular photocyclo-addition of ethylenes to aromatic compounds
R. M. Hochstrasser, Picosecond processes in the isomerism of stilbenes
R. Popovitz-Biro, H. C. Chang, C. P. Tang, N. R. Shochet, M. Lahav and L. Leiserowitz, Stereospecific and regiospecific photoreactions inside the channels of the choleic acids
T. Matsuura, I. Saito, S. Itô, H. Sugiyama, T. Shinmura, Organic chemical approach to photo-crosslinks of nucleic acids to proteins
N. Sutin and C. Creutz, Light induced electron transfer reactions of metal complexes

The Bordeaux research groups organized the nineth Symposium in Pau. The Scientific Chair was Jacques Joussot-Dubien (1929-2009) (Figure 14) and the local organizers were Elisabeth Pocket and Henri Bouas Laurent (Figure 15). In Figure 16 a group of prominent photochemists is seen to enjoy a pre-banquet drink in Pau.

Figure 14. Jacques Joussot-Dubien (1928 – 2009)
From: EPA-Newsletter **62**, p. 23

Figure 15. Elisabeth Poquet and Henri Bouas Laurent (left)
From: H. Bouas Laurent private collection.

Figure 16. In Pau (1982), (from left) Bill Dauben, Stanley Cristol, W. C. Agosta and Ken Houk. From: H. Bouas Laurent private collection.

Photoinduced electron transfer was in 1982 an omnipresent mechanism (the Nobel Prize in Chemistry was awarded to R. *Marcus* in 1992 for the theory of electron transfer) and applications in artificial photosynthesis became important (*Iwao Tabushi*). The lecture by *Horst Kramer* (co-authored by *Rainer Traber* and *Peter Hemmerich*, untimely deceased in October 1981) on electron transfer with triplet flavins represents a milestone in basic flavin photochemistry, the biological importance of which would appear 15-20 years later (*ca.* 2000) when it was discovered that the chromophore in the blue-light photoreceptors (phototropins) in plants is a flavin. The mechanism of action of phototropins *in vivo* involves the photoproduction of the long-lived flavin triplet state, which reacts through an electron transfer mechanism with a cysteine from the apoprotein hosting the flavin, producing a long-lived covalent compound and a concomitant change in the protein structure leading to the transmission of a signal [19]. See *EPA Newsletter* [20].

Table 10. IXth IUPAC Symposium on Photochemistry – Pau – France, 1982. Papers published in [18].

W. C. Agosta and S. Wolff, Photochemistry of carbonyl-substituted hexadienes
H.-D. Becker, On the relationship between molecular geometry and excited state reactivity
Adiabatic photoreactions involving anthracenes
R. A. Beecroft, R. S. Davidson, D. Goodwin and J. E. Pratt, Photo-induced electron transfer reactions - pitfalls and opportunities
P. de Mayo, Superficial photochemistry
K. N. Houk, Theory of cycloadditions of excited aromatics to alkenes
R. Traber, H. E. A. Kramer and P. Hemmerich, One and two electron transfer pathways in the photoreduction of flavin
J. Lemaire, The photocatalyzed oxidation of polyamides and polyolefins
F. D. Lewis, J. L. Buechele, P. A. Teng and E. Weitz, Infrared multiphoton isomerization and fragmentation reactions of organic molecules
T. Matsuo, Photoinduced electron-transfer reactions in membrane and polymer systems for solar energy conversion
U. Mazzucato, Photophysical and photochemical behaviour of stilbene-like molecules and their aza-analogues
H. Morrison, A. Miller, B. Pandey, G. Pandey, D. Severance, R. Strommen and B. Bigot, Photoactivation of remote functional groups in organic molecules and "HOMO dictated" carbonyl photochemistry
I. Tabushi, Artificial photosynthesis. Mechanism and application

Figure 17. David Whitten, From: Guest Book Max Planck Institute for Radiation Chemistry, and **Figure 18.** David Whitten running

David Whitten (Figures 17 and 18, which shows him performing his preferred activity: running) chaired the tenth IUPAC Symposium on Photochemistry in Interlaken in 1984. The local organizer was *André Braun* (Figures 19 and 20).

Figure 19. André Braun

Figure 20. During the free afternoon in Interlaken, 1984, from left: Marie Therese Maurette, Esther Oliveros, André Braun and Diego Armesto.

Table 11. Xth IUPAC Symposium on Photochemistry – Interlaken – Switzerland, 1984. Selected titles from the papers published in [21].

S. E. Braslavsky, The photophysics and photochemistry of the plant photosensor pigment phytochrome
R. A. Caldwell, Intersystem crossing in organic photochemical intermediates
G. Cilento, Generation of electronically excited triplet species in biochemical systems
D. F. Eaton, Electron transfer induced photofragmentation as a route to free radicals
E. Haselbach and T. Bally, Light induced processes in organic molecular ions
A. Henglein, Catalysis of photochemical reactions by colloidal semiconductors
W. H. Laarhoven, Aspects of the photochemistry of aryl ethylenes
J. P. Malrieu, I. Nebot-Gil and J. Sánchez-Marin, Neutral versus ionic excited states of conjugated systems; their role in photoisomerizations
N. Mataga, Photochemical charge transfer phenomena – picosecond laser photolysis studies
S . Tazuke and N. Kitamura, A strategy for mimicking photosynthesis
M. A. Winnik, Fluorescence in structured media: a look at polymer colloids
J. Wirz, Spectroscopic and kinetic investigations of conjugated biradical intermediate

Figure 21. Dick Weiss during the excursion on Wednesday, Interlaken, 1984, private collection SEB

Egbert Havinga opened the Symposium with a lecture on the history of the Symposia on the occasion of the 20th anniversary and there was a concert offered by the photochemists David Schuster, piano, and Frank Mallory, clarinet. George Hammond gave an overview lecture with the title: "Where are the Horizons of Photochemistry Now?" Many talks dealt with photoinduced electron transfer reactions and the mimicking of photosynthesis continued to engage photochemists (again a group from Japan). A workshop on lasers and their applications chaired by Jacques Joussot-Dubien attracted many participants. There were workshops also on "Mechanisms of isomerization of olefines and polyenes" organized by Jack Saltiel, "Micellar and related systems as a medium in photochemistry" organized by A. Lattes, "Self-organization in photochemical systems" organized by J.-C. Micheau, and "Determination of photochemical quantum yields" by Günter Gauglitz. Richard (Dick) Weiss (Figure 21) evidently enjoyed the Symposium and also the excursion day thoroughly. See EPA Newsletter [22].

The eleventh Symposium was chaired by *Frank Wilkinson* (Figure 22) in Lisbon. Local organizer was *Silvia M. B. Costa* (Figure 23)

Table 12. XIth IUPAC Symposium on Photochemistry – Lisbon – Portugal, 1986. Papers published in [23].

G. Porter, Photosynthesis - the first nanosecond
S. J. Formosinho, Radiationless transitions and photochemical reactivity
M. Hasegawa, Topochemical photopolymerization of diolefin crystals
A. Heller, Optically transparent metallic catalysts on semiconductors
T. J. Meyer, Photochemistry of metal coordination complexes: metal to ligand charge transfer excited states
D. Oelkrug, W. Flemming, R. Fullemann, R. Gunther, W. Honnen, G. Krabichler, M. Schafer and S. Uhl, Photochemistry on surfaces
N. J. Turro, Photochemistry of organic molecules in microscopic reactors
F. Bolletta and S. Bonafede, Chemiluminescence and electrochemiluminescence of coordination compounds
M. Demuth, Synthesis of natural products based on photochemical key transformations
R. O. Loutfy, Fluorescence probes for polymer free-volume
C. Pac, Mechanisms and structure-reactivity relationships in photosensitized reactions of some diarylcyclobutanes and quadricyclane by organic electron acceptors
J.-P. Pete, Françoise Henin, R. Mortezaei, J. Muzart and O. Piva, Enantioselective photodeconjugation of conjugated esters and lactones
K. S. Peters, Time-resolved photoacoustic calorimetry

A. Roloff, K. Meier and M. Riediker, Synthetic and metal organic photochemistry in industry
J. C. Scaiano and L. J. Johnston, Photochemistry of reaction intermediates
T. B. Truong, Effect of solvent reorganization on the electron transfer (ET) reaction between donor-acceptor pairs in solution
J. W. Verhoeven, Through-bond charge transfer interaction and photoinduced charge separation
R. O. Loutfy, A.-M. Hor, C.-K. Hsiao, G. Baranyi, P. Kazmaier, Organic photoconductive materials

Figure 22. Frank Wilkinson, 1986.

Figure 23. left: Silvia Braslavsky, right: Silvia Costa, Lisbon, 1986

Figure 24. Vincenzo Balzani

George Porter (Chemistry Nobel Laureate in 1967) (1920-2002) elaborated on the studies with fast spectroscopic methods on photosynthetic units and antennas. The results of many years of his group's investigations of photoreactions in confined systems, in particular in zeolites, were reviewed by *Nicholas (Nick) Turro*. *Jan Verhoeven* presented the studies of his group on photoinduced charge transfer across donor-bridge-acceptor supermolecular systems with various types of interconnecting bridges. Four panels organized in two parallel sessions discussed "Photochemical reactivity, electron and proton transfer" chaired by *Albert Weller*, "Mechanistic aspects of organic photochemistry" chaired by *Anthony Trozzolo*, "Photochemical reactions in organized media" chaired by *J. Kerry Thomas*, and "Photoimaging, photoresists and photopolymerization" led by *Ed Chandross*. See [24].

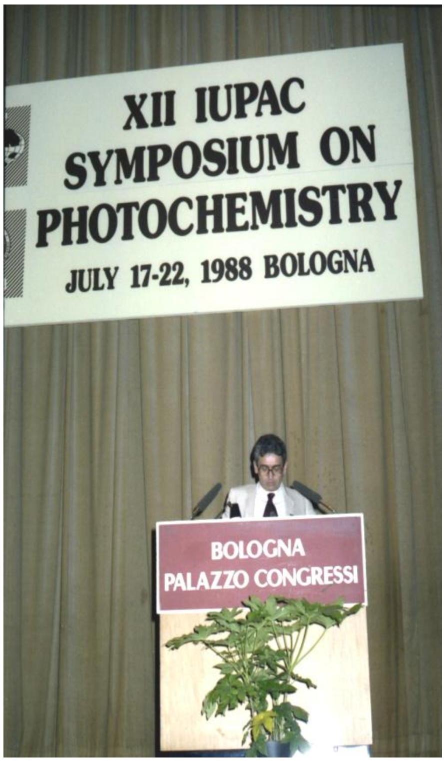

Figure 25. Inauguration of the XIIth Symposium.

The twelfth IUPAC Symposium on Photochemistry, chaired by *Vincenzo Balzani* (Figure 24) in 1988 was a very special moment in the history of the symposia series and the photochemical community. The Symposium took place at the University of Bologna, which was commemorating the 900th Anniversary of its inauguration (Figure 25) and the Porter Medal, the highest Award in the photochemical community, presented by the EPA, the I-APS and the Asian and Oceania Photochemistry Association (APA), was instituted [25]. *Lord George Porter* (Figure 26) was the first awardee. *Heinz Roth* dedicated his lecture to the work of *Giacomo Ciamician* (1857-1922), the prominent photochemist of Bologna and one of the fathers of photochemistry. Coinciding with the Symposium, the University of Bologna presented the first Giacomo Ciamician Medal to *Albert Weller* [26]. *Fabrizio Bolletta* was the local organizer of this Symposium.

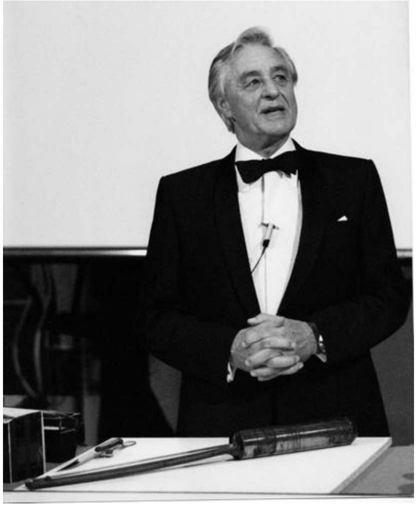

Figure 26. Lord George Porter (1920 – 2002)
From: Photochem. Photobiol. Sci., (2002) **1**, vi-vii

Table 13. XIIth IUPAC Symposium on Photochemistry – Bologna – Italy, 1988. Papers published in [27].

H. D. Roth, Magnetic resonance methods in the mechanistic photochemistry of ketones, olefins, and oximes
J. D. Coyle, Electron-transfer photochemistry of organic amides and imides
J. R. Huber, Photodissociation of molecules: the microscopic path of a molecular decay
H. Michel and J. Deisenhofer, Structure and function of the photosynthetic reaction center from *Rhodopseudomonas viridis*
J. Michl et al, Solution photochemistry of poly(dialkylsilanes): a new class of photoresists
F. Scandola and M. T. Indelli, Second sphere donor acceptor interactions in excited states of coordination compounds. Ruthenium(II) bipyridine cyano complexes
A. G. Schultz, New photochemistry of 2,5-cyclohexadien-1-ones and related compounds
T. Arai, T. Karatsu, H. Misawa, Y. Kuriyama, H. Okamoto, T. Hiresaki, H. Furuuchi, H. Zeng, H. Sakuragi and K. Tokumaru, Novel insights into photoisomerization of olefins
R. G. Weiss, R. L. Treanor and A. Nuñez, Norrish II reactions of rod-like ketones in ordered media comprised of rod-like layered solvent molecules
A. Albini and E. Fasani, Interaction between photoexcited naphthalenenitriles and dienes: addition and sensitization
M. A. Fox, Photoinduced electron transfer in arranged media and on semiconductor surfaces
F.-W. Grevels, J. Jacke, W. E. Klotzbücher, S. Özkar and V. Skibbe, Photoreactions of group 6 metal carbonyls with olefins
T. Shimidzu, T. Iyoda and K. Honda, Some aspects of electron transfer sensitization systems
H.-J. Timpe, Photoinitiator systems for concurrent radical and cationic polymerization
K. I. Zamaraev, S. V. Lymar, M. I. Khramov and V. N. Parmon, Vectorial phototransfer of electrons across lipid membranes

The Nobel Prize in Chemistry was awarded in 1988 to *Harmut Michel, Johann Deisenhofer* and *Robert Huber* for the determination of the structure of the bacterial reaction centre. The structure of PSII underscored the concept that one goal for achieving the mimicking of photosynthesis was (and still is) the compartmentalization of the various electron transfer steps and the control of the vectorial electron transfer process. Thus, several contributions focussed on the behaviour of organized environments. *Richard (Dick) Weiss* showed how the order of the solvent environment influences the Norrish II photochemical reaction, *Marye-Anne Fox* demonstrated the possibility of photoinduction of electron transfer through thick layers using various types of structures and *Kirill Zamaraev* (1939-1996, president of IUPAC 1994 -1995) analysed the vectorial transfer across lipid membranes. *Ahmed Zewail* (Chemistry Nobel Laureate in 1999) showed the capabilities of femtosecond pulses and detection of transient absorption by a delayed beam (pump-probe as we call the technique today) to observe the dynamics of transition states. I believe that this was the first lecture on femtosecond spectroscopy in an IUPAC Symposium. There were again four panel discussions in two parallel sessions. *Nick Serpone* chaired the Panel on “Photochemistry and the Environment”, *Howard Zimmerman* led the Panel on “Interaction of Theory and Experiment in Organic Photochemistry”, Jean-Marie Lehn (Chemistry Nobel Laureate in 1987) chaired the Panel on “Supramolecular photochemistry”, and André Braun one on an “Up-date on the technology of preparative photochemistry”. For a report on the Symposium see [28].

Figure 27. Fred Lewis
From: Guest Book, Max Planck Institute for Radiation Chemistry

Table 14. XIIIth IUPAC Symposium on Photochemistry – Coventry – UK. 1990. Papers published in [29].

M. Kasha (Porter Medal), Four great personalities of science: G. N. Lewis, J. Franck, R. S. Mulliken and A. Szent-Gyorgyi

V. Balzani, L. De Cola, L. Prodi and F. Scandola, Photochemistry of supramolecular species

A. M. Braun and E. Oliveros, Applications of singlet oxygen reactions: mechanistic and kinetic investigations

H. Dürr, A new photochromic system - potential limitations and perspectives

N. P. Ernsting, B. Dick and Th. Arthen-Engeland, The primary photochemical reaction step of unsubstituted indolino-spiropyrans

H. Hennig, D. Rehorek, R. Stich and L. Weber, Photocatalysis induced by light-sensitive coordination compounds

M. Irie, Properties and applications of photoresponsive polymers

E. Lissi, M. A. Rubio, $O_2(^3\Sigma)$ and $O_2(^1\Delta)$ processes in microheterogenous systems

K. Maruyama and A. Osuka, A chemical approach toward photosynthetic reaction center

P. Mathis, Primary processes in photosynthetic reaction centers

T. Miyashi, H. Ikeda, A. Konno, O. Okitsu and Y. Takahashi, Photoinduced electron-transfer reactions of the cope and related systems

R. N. Perutz, S. T. Belt, A. McCamley and M. K. Whittlesey, C-H activation by organometallics: the role of matrix isolation studies

R. Z. Sagdeev and E. G. Bagryanskaya, Stimulated nuclear polarization - a new method for studying the mechanisms of photochemical reactions

J. C. Scaiano, V. Wintgens and J. C. Netto-Ferreira, Mechanistic studies of the photogeneration and photochemistry of *ortho*-xylylenes

G. B. Schuster, Photochemistry of organoborates: intra-ion pair electron transfer to cyanines

J. P. Simons, Stereodynamics of molecular photodissociation

> *R. Srinivasan, B. Braren and K. G. Casey,* Ultraviolet laser ablation and decomposition of organic materials

J. W. Verhoeven, Electron transport *via* saturated hydrocarbon bridges: 'exciplex' emission from flexible, rigid and semiflexible bichromophores

P. A. Wender, R. Ternansky, M. deLong, S. Singh, A. Olivero and K. Rice, Arene-alkene cycloadditions and organic synthesis

X. Coqueret, A. Hajaiej, A. Lablache-Combier, C. Loucheux, R. Mercier, L. Pouliquen and L. Randrianarisoa-Ramanantsoa, Synthesis and properties of photoreactive polysiloxanes containing pendant functional groups

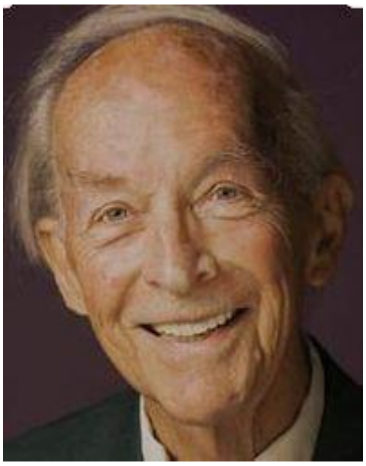

Figure 28. Michael Kasha (1920 – 2013)
From Wikipedia

Fred Lewis (Figure 27) chaired the thirteenth IUPAC Symposium on Photochemistry in the University of Warwick, Coventry. R. S. Davidson was the local organizer - and for several years the editor of the issues of Pure and Applied Chemistry collecting the papers from the Symposia on Photochemistry. *George Porter* presented the Porter Medal to *Michael Kasha* (1913-2013) (Figure 28) [30], who gave a lecture on four major scientific personalities. *Niko Ernsting* showed the decay of photoproduced species with a time resolution of ca. 400 fs, using a pump-probe spectrometer with 260-fs pump pulses. *K. Maruyama* discussed the effect of orientation on the charge transfer after excitation of conformationally restricted dimeric porphyrins (as biomimetic models of photosynthetic units), using picosecond time-resolved transient absorption spectroscopy with a time resolution of 26 ps and fluorescence decay with a time resolution of 1 ns. *Jan Verhoeven* showed the variable interaction between chromphores linked by different bridges.

Figure 29. (from left) Jorge Tocho, Eduardo Lissi, Silvia Braslavsky, Miguel Neumann, Pedro Aramendía and Juan (Tito) Scaiano. University of Warwick, 1990.

Figure 30. Denis De Keukeleire, hopfen chemical expert. From http://belgium.beertourism.com/blog/professor-denis-de-keukeleire-hop-is-hip

During a coffee break a photographer from the company ICI, who was using a novel electronic camera, took a picture of the Argentinian group present. I cannot avoid showing it here (Figure 29). *P. Gregory* from ICI discussed the technique in a lecture within a workshop with two additional industrial presentations, one on "Stereolithography", and another one on "Colour Imaging". For a review of the Symposium see [31].

Table 15. XIVth IUPAC Symposium on Photochemistry – Leuven – Belgium, 1992. Papers published in [32].

K. Honda (Porter Medal), From Photoelectrochemistry to Photocatalysis

A. U. Acuña, J. González-Rodríguez, M. P. Lillo, C. R. Mateo, K. Razi Naqvi, Micro and nanosecond detection of biomolecular dynamics by polarized luminescence

A. E. Johnson, N. E. Levinger, D. A. V. Kliner, K. Tominaga, P. F. Barbara, Ultrafast experiments on the role of vibrational modes in electron transfer

K. W. Allen, E. S. Cockburn, R. S. Davidson, K. S. Tranter and H. S. Zhang, Some new developments in radiation curing

J.-P. Desvergne, F. Fages, H. Bouas-Laurent and P. Marsau, Tunable photoresponsive supramolecular systems

J. M. J. Fréchet, The photogeneration of acid and base within polymer coatings: Approaches to polymer curing and imaging

Z. R. Grabowski, Electron transfer and the structural changes in the excited state

H. B. Gray and J. R. Winkler, Photoinduced electron transfer in ruthenium-modified cytochrome *c*

I. Weissbuch, R. Popovitz-Biro, J.-L. Wang, G. Berkovic, L. Leiserowitz and M. Lahav, Structure and dynamics of amphiphilic aggregates at air/solution interfaces en route to crystal formation

F. D. Lewis, D. M. Bassani and G. Dasharatha Reddy, Styrene-amine and stilbene-amine intra-molecular addition reactions

H. Masuhara, Laser microchemistry

R. W. Matthews, Photocatalytic oxidation of organic contaminants in water: An aid to environmental preservation

R. D. Miller, M. Baier, A. F. Diaz, E. J. Ginsburg and G. M. Wallraff, The electronic structure of high molecular weight substituted silane polymers in solution: Fluorescence quenching studies

A. A. Lin, C.-F. Chu and W.-Y. Huang, Reactant preordering in solid photopolymers

I. Saito, Photochemistry of highly organized biomolecules: Sequence-selective photoreaction of DNA

A. Vogler and H. Nikol, Photochemistry and photophysics of coordination compounds of the main group metals

M. R. Wasielewski, M. P. O'Neil, D. Gosztola, M. P. Niemczyk and W. A. Svec, Ultrafast photoinduced electron transfer reactions in supramolecular arrays: From charge separation and storage to molecular switches

D. Andrew, D. J. Hastings, D. L. Oldroyd, A. Rudolph, A. C. Weedon, D. F. Wong and Boke Zhang, Triplet 1,4-biradical intermediates in the photocycloaddition reactions of enones and N-acylindoles with alkenes

U. P. Wild, S. Bernet, B. Kohler and A. Renn, From supramolecular photochemistry to the molecular computer

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Frans De Schryver (see Figure 12) chaired the fourteenth Symposium. *Denis De Keukeleire* (the beer expert in the crew) was the local organizer (Figure 30).

There were 450 participants in this Symposium (many of whom enjoyed great beer after the sessions) and I believe it was the first one in which parallel sessions of the invited lectures and selected oral contributions had to be arranged. The following Symposia all had parallel sessions to accommodate the presentations of the increasing number of participants.

Kenishi Honda received the Porter Medal from the hands of *George Porter* for his work on photochemistry, photography, and electrochemistry, as reviewed in the presentation address by *Frank Wilkinson* [33]. *Harry Gray* discussed their studies on photoinduced electron transfer from excited Ru(ammine) complexes attached to histidine at various distances from the acceptor cytochrome c and of Zn-substituted cytochrome c. *Urs Wild* demonstrated the possibilities of data storage using hole burning techniques. The Bordeaux group presented their progress in the studies on supramolecular systems and *Paul Barbara* (1953-2010) showed the use of ultrafast techniques (pulse-limited to > 100 fs) to study intra- and intermolecular electron transfer processes. *Hiroshi Masuhara* demonstrated the use of a multi-beam laser scanning micro-manipulation system to study the reactions of isolated particles of various materials. One of the invited lectures was on the role of hydrophobic and lipophobic effects on photoinduced processes by *C.-H. Tung* from the Academia Sinica in Beijing. There were several presentations by scientists working in industrial environments, such as *Ian Gould* from Eastman Kodak, *R. D. Miller* from IBM (San Jose), *K. Dietliker* from Ciba-Geigy (Fribourg), and *J. W. Ketellapper* from Agfa-Gewaert. For a report on the Symposium see [34].

Figure 31. Josef Michl,
Guest Book, Max Planck Institute for Radiation Chemistry

Josef Michl (Figure 31) was the Scientific Chair of the fifteenth Symposium in 1994 in Prague, Czech Republic. *I. Stibor* was the local organizer. This time 600 participants took part in the Symposium. There was a very strong participation of colleagues from the European "Eastern Countries".

Table 16. XVth IUPAC Symposium on Photochemistry – Prague, 1994. Papers published in [35].

N. J. Turro (Porter Medal) Supramolecular organic and inorganic photochemistry: Radical pair recombination in micelles, electron transfer

M. Allan, What can electron impact spectroscopy offer to photochemistry? Triplet states, negative ions and intramolecular electron transfer

R. S. Becker, J. Seixas de Melo, A. L. Maçanita and F. Elisei, Comprehensive investigation of the solution photophysics and theoretical aspects of oligothiophenes of 1-7 rings

F. Bernardi, M. Olivucci and M. A. Robb, Following reaction paths in organic photochemistry: The special role of surface crossings on starburst dendrimers, and the use of DNA as a molecular wire

N. Buhler and D. Bellus, Photopolymers as a powerful tool in modern technology

D. M. Burland, G. C. Bjorklund, W. E. Moerner, S. M. Silence and J. J. Stankus, Photorefractive polymers - A status report

R. H. Crabtree, Mercury-photosensitized reactions

C. Creutz, J.-S. Song and R. M. Bullock, Photoinduced atom-transfer reactions between transition-metal centres

J. Gebicki, Low barrier isomerization processes in radical cations

H. J. C. Jacobs, Photochemistry of conjugated trienes: Vitamin D revisited

L. J. Johnston and N. P. Schepp, Laser flash photolysis studies of the reactivity of styrene radical cations

N. Kitamura, K. Nakatani and H.-B. Kim, Spectroscopic and electrochemical analyses of electron transfer and mass transfer across the microdroplet/solution interface

W. Knoll, Integrated optics for the characterization of photoreactive organic thin films

K. R. Mann, A. M. Blough, J. L. Schrenk, R. S. Koefod, D. A. Freedman and J. R. Matachek, Mechanistic aspects of the photochemistry of [CpM(η6-arene)]+ complexes of Fe, Ru and Os

J. P. Mittal, Excited states and electron transfer reactions of fullerenes

H. Morrison, K. Agyin, A. Jiang and C. Xiao, Photochemical activation of distal chromophores by antenna substituents in polyfunctional molecules

D. Phillips, The photochemistry of sensitisers for photodynamic therapy

C. M. Previtali, Solvent effects on intermolecular electron transfer processes

N. Sabbatini, M. Guardigli, I. Manet, R. Ungaro, A. Casnati, R. Ziessel, G. Ulrich, Z. Asfari and J.-M. Lehn, Lanthanide complexes of encapsulating ligands: Luminescent devices at the molecular level

J. Santamaria, Photoinduced electron transfer in organic synthesis: Application to alkaloids

M. A. El-Sayed, Jennifer Griffiths, L. Song and N. Zhang, On the molecular mechanisms of the rapid and slow solar-to-electric energy storage processes by the other natural photosynthetic system, bacteriorhodopsin

F. C. De Schryver, N. Boens, M. Van der Auweraer, L. Viaene, S. Reekmans, B. Hermans, J. Van Stam, M. Gehlen, H. Berghmans and M. Ameloot, Excited-state probing of associative and covalent macromolecules

H.-J. Wolff, D. Burssher and U. E. Steiner, Spin-orbit coupling controlled spin chemistry of Ru(bpy)32+ photooxidation: Detection of strong viscosity dependence of in-cage backward electron transfer rate

G. E. Johnson, K. M. McGrane and M. Stolka

Electroluminescence from single layer molecularly doped polymer films

J.-S. Taylor, DNA, sunlight and skin cancer

H. P. Trommsdorff, A. Corval and L. von Laue, Spectral hole burning: Spontaneous and photoinduced tunneling reactions in low temperature solids

I. Yamazaki and N. Ohta, Photochemistry in LB films and its application to molecular switching devices

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Figure 32. George Porter gives the Porter medal to Nick Turro.
Foto: Jan Verhoeven

Figure 33. Tito Scaiano receiving the Porter Medal from George Porter. London, 1995. Private collection SEB.

George Porter himself handed the Porter Medal to *Nick Turro* (Figure 32), *Nanda Sabbatini* showed the results of studies with luminescent lanthanides performed in the group around *Jean-Marie Lehn*, and *F. Bernardi* explained some of the novel quantum chemical calculations made together with *Massimo Olivucci* and *Mike Robb* on reaction trajectories from excited states. *Frans De Schryver* demonstrated the use of various emission techniques for the study of inter- and intra-molecular interactions in complex media.

Photobiology was well represented in this Symposium. Mostafa El-Sayed presented mechanistic studies on bacteriorhodopsin, including subpicosecond transient absorption decay of the excited bacteriorhodopsin and some of its mutants. There were 45 papers focusing on photobiology including 4 of the plenary lectures. The 455 posters covered all areas of basic and applied photochemistry. A report on the Symposium was published in [36].

The Porter Medal has in general been awarded during the IUPAC Symposia, with one exception. In 1995, during the International Conference on Photochemistry held in London, the Porter Medal was awarded to *Juan C. (Tito) Scaiano*, as well directly handed by *George Porter* (Figure 33) [37].

Figure 34. Jakob (Joggi) Wirz. From: Photochem. Photobiol. Sci., (2002) **1**, 441-458

In 1996 *Jakob (Joggi) Wirz* (Figure 34) chaired the sixteeth IUPAC Symposium in Helsinki, Finland, with *Helge Lemmetyinnen* (Figure 35) as the local organizer.

Figure 35. Helge Lemmetyinen (right) passes the duties to Richard Caldwell who would be the scientific chair of the 17th IUPAC Symposium on Photochemistry in Sitges, Barcelona in 1998. Private collection SEB.

Figure 36. Left: Henry Linschitz (1919 – 2014), a pioneer in Photochemistry, with Klaas Zachariasse in Helsinki, 1996. Private collection SEB.

Henry Linschitz (1919-2014) (in Figure 36 with *Klaas Zachariasse*) showed a poster in which various mechanisms for benzophenone triplet quenching by metal ions and cyano complexes were described in detail. He also co-authored a lecture and chaired a session.

Table 17. XVI IUPAC Symposium on Photochemistry – Helsinki – Finland, 1996. Papers published in [38].

N. Mataga (Porter Medal), Development of exciplex chemistry: Some fundamental aspects
W. Adam, C. van Barneveld, O. Emmert, H. M. Harrer, F. Kita, A. S. Kumar, W. Maas, W. M. Nau, S. H. K. Reddy and J. Wirz, About monoradicals, triplet diradicals and higher spin states: Understanding electronic substituent effects through EPR and time-resolved UV spectroscopy
F. Kulzer, R. Kettner, S. Kummer and Th. Basché, Single molecule spectroscopy: Spontaneous and light-induced frequency jumps
M. A. El-Sayed and S. Logunov, On the molecular origin of the protein catalysis of the primary process in bacteriorhodopsin photosynthesis: Retinal photoisomerization
L. Peng, C. Colas and M. Goeldner, Photoregulation of cholinesterase activity
L. B.-Å. Johansson and J. Karolin, Electronic energy migration and rotation within bichromophoric molecules
J. M. Kelly, M. M. Feeney, L. Jacquet, A. Kirsch-De Mesmaeker and J.-P. Lecomte, Photoinduced electron transfer between ruthenium complexes and nucleotides or DNA
M. Klessinger, Theoretical models for the selectivity of organic singlet and triplet photoreactions
G. Marconi and B. Mayer, Conformational and circular dichroism studies on cyclodextrin inclusion complexes
J. Michl and Z. Havlas, Spin-orbit coupling in biradicals: Structural aspects
M. G. Neumann and M. J. Tiera, Photochemical determination of the interactions between surfactants and polyelectrolytes
A. Osuka, N. Mataga and T. Okada, A chemical approach towards the photosynthetic reaction center
M. S. Platz, H. Huang, F. Ford and J. Toscano, Photochemical rearrangements of diazirines and thermal rearrangements of carbenes
H. D. Roth, H. Weng, D. Zhou and T. Herbertz, Electron transfer photochemistry of bifunctional strained-ring and unsaturated systems
M. Leibovitch, G. Olovsson, J. R. Scheffer and J. Trotter, Absolute configuration correlation studies in solid state organic photochemistry
H. Shizuka, Photophysics and photochemistry of triplet exciplexes between triplet naphthalene derivatives and benzophenone

D. J. Stufkens, M. P. Aarnts, B. D. Rossenaar and A. Vlcek, Jr, A new series of Re- and Ru-complexes having a lowest σπ* excited state that varies from reactive to stable and long lived

H. Tomioka, Matrix isolation study of reactive o-quinoid compounds: Generation detection and reactions

J. Troe, Towards a quantitative characterization photoisomerization rates

C. Wentrup, A. Reisinger, G. G. Qiao and P. Visser, Photochemistry of pyridyl azides and diazo ketones in matrix and in solution

> *F. Wilkinson*, Quenching of electronically excited states by molecular oxygen in fluid solution

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Figure 37. Jakob (Joggi) Wirz and wife during the banquet. Helsinki 1996. Private collection SEB

The recipient of the Porter Medal was *Noboru Mataga* (1927-2011) (Figure 38) [39]. *Waldemar Adam* (Figure 39) presented an inspiring and entertaining plenary talk including the collaborations with several laboratories. *Thomas Basché* explained the possibilities of single molecule spectroscopy (SMS) to study host-matrix interactions in solids at low temperatures, whereas *John Sheffer* analysed the possibilities and methods used when studying photochemistry in solid samples. *Martin Klessinger* and *Josef Michl* showed in their respective presentations the advances in the capabilities of calculations of structures and trajectories.

I was asked to organize a workshop on "Photothermal Methods" within the frame of the Symposium. Contributors were *R.*

Figure 38. Noboru Mataga (1927 - 2011)

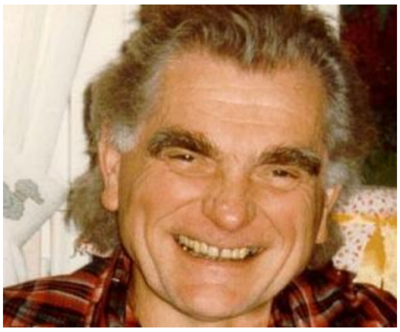

Figure 39. Waldemar Adam

J. Dwayne Miller, *Mathew Zimmt, Erich Vautey, Thomas Gensch, Cristiano Viappiani,* and *Reinhard Schmidt*. The discussion was very lively. There were two other parallel workshops, one on "Photochemical Methods for the Oxidative Degradation of Organic Pollutants" chaired by *Jim R. Bolton* and *André A. Braun* and another one on "Photopolymerization" chaired by *K. Dietliker* and *D. C. Neckers*.

At the end of the Symposium a Round Table discussion on "The Future of Photochemistry" was organized by *Ed Chandross* who moderated the very participative discussion. As we know, the future is very unpredictable. The present (2015) very healthy and productive (basic and applied, theoretical and instrumental, biological and in material sciences) photochemistry shows that its future was and still is very promising. A report on the Symposium was published in [40].

Figure 40. Collaborators (fomer and contemporary) of Braslavsky in Helsinki, 1996. From left: Thomas Gensch, Pedro Aramendía, Cristina Martí, Claudio Borsarelli, Santi Nonell, Ana Paré. Private collection SEB.

The photo in Figure 40 shows my collaborators (former and contemporary) who attended the Symposium in Helsinki. After the Symposium, *Claudio Borsarelli* and I went hiking to the very North of Finland, to a National Park on the border between Sweden, Norway, and Finland. It was a wonderful week, camping and hiking on the way to the North, enjoying the long Finish summer nights, the lakes, the soft hills, the great huts, the saunas, the strawberries, and fighting the mosquitoes. I learned that several participants of the Symposium also enjoyed all the above wonders, including the mosquitoes.

Sitges, in the Catalan coast of Spain, was the site of the seventeenth IUPAC Symposium on Photochemistry, chaired by *Richard (Dick) Caldwell* (Figure 41) and locally organized by a group of Spanish photochemists led by *Josep Font* (see Figure 42) with *José Luis Bourdelande*, *Santi Nonell*, and *Carmen Brosa*. I attended this meeting in a wheel chair, because I had broken a leg while hiking in Canada, some time before the Sitges meeting. But that is another story.

Figure 41. Richard (Dick) Caldwell

Figure 42. From left: Josep Font, Guillermo Orellana, Ulises Acuña in Helsinki, 1996. Private collection SEB.

Table 18. XVIIth IUPAC Symposium on Photochemistry – Sitges, 1998. Papers published in [41].

F. C. De Schryver (Porter Medal), Time, space and spectrally resolved photochemistry from ensembles to single molecules

Y. Atassi, J. Chauvin, J. A. Delaire, J.-F. Delouis, I. Fanton-Maltey and K. Nakatani, Photoinduced manipulations of photochromes in polymers: Anisotropy, modulation of the NLO properties and creation of surface gratings

C. Heinemann, X. Xing, K.-D. Warzecha, P. Ritterskamp, H. Görner and M. Demuth, An asymmetric induction principle and biomimetics with photons via electron transfer

A. Fujishima and T. N. Rao, Interfacial photochemistry: fundamental and applications

D. Gust, T. A. Moore and A. L. Moore, Mimicking bacterial photosynthesis

E. S. Medvedev and A. A. Stuchebrukhov, Dynamic effects in long-distance biological electron transfer reactions

R. N. Perutz, Metal dihydride complexes: Photochemical mechanisms for reductive elimination

J. Wirz, Kinetics of proton transfer reactions involving carbon

Frans De Schryver (Figure 12) [42] received the Porter Medal. *Marye-Anne Fox* and *Franco Scandola* presented invited lectures in a session dedicated to *Francesc Trull*, member of the organizing committee of the Symposium, a dear friend, and organic photochemist from Barcelona whose untimely early death in 1997 meant a sad personal and scientific loss. A session organized by *Claus Seidel* dealt with single molecule fluorescence spectroscopy and imaging (three lectures by *Claus Seidel, Richard A. Keller, and Alfred J. Meixner*) and fluorescence correlation spectroscopy (*J. Widengren*). *Willi Sundstroem* discussed the studies of his group on femto- and picosecond times of photoinduced reactions in small molecules and in chromophores of biological importance. *Christoph Richter*, from the Plataforma Solar de Almería, reviewed the "Photochemical Applications of Sunlight for Fine Chemical Synthesis", and *Devens Gust* summarized the studies from the group at Arizona State University towards man-made photosynthesis. *William Wilson* presented progress in volume holography and *Jacques Delaire* on photochromic polymers. In summary, great examples of applications of spectroscopy and photochemistry. Not all plenary and invited lectures were published in *PAC*. A report on the Symposium was published in [43].

Figure 43. Silvia Braslavsky

I (Figure 43) had the pleasure of chairing the eighteenth IUPAC Symposium on Photochemistry in Dresden in 2000, with the enormous help of *Thomas Wolff* (Figure 44) as a local organizer.

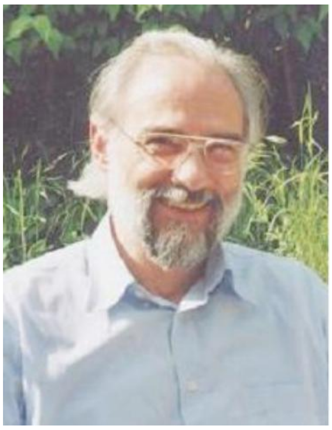

Figure 44. Thomas Wolff

Table 19. XVIIIth IUPAC Symposium on Photochemistry – Dresden - Germany, 2000. Papers published in [44].

V. Balzani (Porter Medal)

H. D. Roth, Twentieth century developments in photochemistry. Brief historical sketches

D. E. Wetzler, C. Chesta, R. Fernández-Prini and P. F. Aramendía, Dynamic solvatochromism in solvent mixtures

F. Fages, S. Leroy, T. Soujanya and J.-E. Sohna, Photoactive pyrene-containing receptors for transition-metal ions

J. Fidy, M. Laberge, B. Ullrich, L. Polgar, Z. Szeltner, J. Gallay and M. Vincent, Tryptophan rotamers that report the conformational dynamics of proteins

L. Flamigni, Charge separation and energy transfer in multicomponent porphyrinic arrays

R. H. Friend, Conjugated polymers. New materials for optoelectronic devices

T. Gensch, K. Tsuda, G. C. Dol, L. Latterini, J. W. Weener, A. P. H. J. Schenning, J. Hofkens, E. W. Meijer and F. C. De Schryver, Microscopy and optical manipulation of dendrimer-built vesicles

G. I. Childs, D. C. Grills, Xue Z. Sun and M. W. George, Organometallic alkane and noble-gas complexes in conventional and supercritical fluids

B. Giese, M. Spichty and S. Wessely, Long-distance charge transport through DNA. An extended hopping model

I. R. Gould, J. R. Lenhard, A. A. Muenter, S. A. Godleski and S. Farid, New approach to silver halide photography using radical cation chemistry

M. Grätzel, Molecular Dynamics that mimic photosynthesis

A. R. Holzwarth, M. Katterle, M. G. Müller, Y.-Z. Ma and V. Prokhorenko, Electron-transfer dyads suitable for novel self-assembled light-harvesting antenna/electron-transfer devices

M. F. García-Parajó, J.-A. Veerman, L. Kuipers and N. F. van Hulst, Looking at the photodynamics of individual fluorescent molecules and proteins

Y. Inoue, Norimitsu Sugahara and Takehiko Wada, Vital role of entropy in photochirogenesis

M. A. Miranda, Photosensitization by drugs

G. K. Moortgat, Important photochemical processes in the atmosphere

M. Nowakowska, M. Kepczynski and K. Szczubialka, New polymeric photosensitizers

Y. Li, C. E. Whittle, K. A. Walters, K. D. Ley and K. S. Schanze, Photophysics of π-conjugated metal-organic oligomers

A. Prasanna de Silva, D. B. Fox, T. S. Moody and S. M. Weir, Luminescent sensors and photonic switches

M. Terazima, Protein dynamics detected by the time-resolved transient grating technique

S. Tero-Kubota, Singlet and triplet energy splitting in the radical ion pairs generated by photoinduced electron-transfer reactions
R. de Vivie-Riedle, L. Kurtz and A. Hofmann, Coherent control for ultrafast photochemical reactions
P. Wan, Darryl W. Brousmiche, C. Z. Chen, J. Cole, M. Lukeman and M. Xu, Quinone methide intermediates in organic photochemistry
I. Willner and B. Willner, Molecular and biomolecular optoelectronics
V. Wing-Wah Yam, Molecular design of luminescent metal-based materials

Vincenzo Balzani received the Porter Medal and held a lecture entitled: "From Supramolecular Chemistry to Molecular-level Devices" [45]. The opening Plenary Lecture was by *Itamar Willner*. *Jacqueline Barton* gave a Plenary Lecture on "Charge transfer through the DNA pair stack" and shared the session with *Bernd Giese* who demonstrated in his Plenary Lecture the sensitivity of the charge transfer process in DNA to the particular arrangement of the bases. After the session a very lively discussion evolved. The number of women offering lectures was larger than in previous Symposia; *Jacqueline Barton*, *Lucia Flamigni*, *María García Parajó*, *Judit Fidy*, *Regina de Vivie-Riedle*, *Maria Nowakowska*, *Gudrun Hermann,* and *Vivian Wing-Wah Yam* gave Plenary or Invited Lectures and a good number of women researchers were chosen to present oral contributions. There were three Workshops, one on "Theoretical Organic (Photo) Chemistry" organized by *Martin Klessinger* and held *in memoriam* of *Mike Zerner*, with the participation of *Yehuda Haas*, *Michael Robb*, and *Tod Martínez*, one on "Primary Processes in Biological Photoreceptors" organized by *Tomas Gillbro* with the participation of *Philip Anfinrud*, *Martin Engelhard*, *Klaas Hellingwerf*, *Gudrun Hermann*, and *Vitally Sineshchekov*, and one on "Solid State Photochemistry" organized by *Miguel García Garibay* with the participation of *Masahiro Irie*, *J. Michael McBride*, *Yushi Ohashi*, and *John Scheffer*. The number of talks and posters dedicated to photobiology was very large. Still, there was a good balance of talks on all areas of photochemistry. *Heinz Roth* offered us a wonderful lecture on historical aspects of the development of photochemistry in the 20th Century and *Kurt Schaffner* gave us his recollections on the history of the IUPAC Symposia on Photochemistry. A report on the Symposium was published in [46].

In 2002 the Symposium in Budapest was chaired by *Heinz Roth* (Figure 45) with *Josef Nyitrai* (Figure 46) as the local organizer.

Figure 45. Heinz Roth,
Guest Book, Max Planck Institute for Radiation Chemistry

Figure 46. Josef Nyitrai, Private collection SEB

Table 20. XIXth IUPAC Symposium on Photochemistry – Budapest – Hungary, 2002. Papers published in [47].

H. A. Fogarty, D. L. Casher, R. Imhof, T. Schepers, D. W. Rooklin and J. Michl (Porter Medal), σ Bonds: Electronic structure, photophysics, and photochemistry of oligosilanes
W. Lubitz, Photochemical processes in photosynthesis studied by advanced electron paramagnetic resonance techniques
H. Tomioka, Triplet carbenes: From fleeting existence to attractive molecular units
K. Mizuno, T. Hayamizu and H. Maeda, Regio- and stereoselective functionalization of electron-deficient alkenes by organosilicon compounds via photoinduced electron transfer
A. M. Brouwer, S. M. Fazio, C. Frochot, F. G. Gatti, D. A. Leigh, J. K. Y. Wong and G. W. H. Wurpel, Photoinduced dynamics in hydrogen-bonded rotaxanes
P. Piotrowiak, K. Deshayes, Z. S. Romanova, C. Pagba, S. Hore, G. Zordan, I. Place and A. Farrán, Electron and excitation transfer in hetero-supramolecular assemblies and at molecule-nanoparticle interfaces
D. M. Guldi, Molecular porphyrin-fullerene architectures
O. A. Fedorova, Y. V. Fedorov, E. N. Andrjukhina, S. P. Gromov and M. V. Alfimov, Cation-dependent photochromic properties of novel ditopic receptors
H. García, Photoresponsive porous organosilicas
S. E. Braslavsky, Electron-transfer reactions studied by laser-induced optoacoustics: Learning about chromophore-medium (protein) interactions

Josef Michl (see Figure 31) received the Porter Medal and was introduced by *Jakob (Joggi) Wirz* [48]. The opening session started with the Plenary Lecture by *Rudolf Rigler* on "Stochastic processes and correlated events: Catalysis by single enzyme molecules", followed by the Invited Lecture by *Eric Vauthey* about "Ultrafast spectroscopic investigations of intermolecular photoinduced electron transfer reactions". There were two parallel workshops, one on "Fast Spectroscopy on Biological Systems" organized by *Eric Vauthey* with the participation of *Mircea Cotlet*, *Abderrazzak Douhal*, *Hiroshi Fukumura*, and *Bern Kohler* and the other one on "Theory and calculations in Photochemistry" organized by *Thomas Bally* with the participation of *Obis Castaño*, *James Hynes*, *Giorgio Orlandi*, and *Michael Kuzmin.* The oral contributions were organized in three parallel sessions. *Bob Liu* reviewed his concept of "Hula-twist as a supramolecular photoisomerization mechanism." Two-photon excitation was the object of a talk by *Seth Marder*. The promising two-photon technologies and applications in medicine were obviously made possible in 2002 by the development of powerful lasers and nowadays of laser diodes. There was a Round Table discussion about the future of photochemistry with *Ed Chandross, Heinz Roth, Frans De Schryver, Josef Michl, and Hiroshi Masuhara.* Again (like 6 years earlier in Helsinki) the point was made that good applications only can arise from excellent research in basic science and good basic science education.

Figure 47 is a snapshot I made from a group of photochemists during the Wednesday excursion. A report on the Symposium was published in [49].

Figure 47. From left: Norbert Hofmann, Horst Kisch, Helmut Görner, (front) Axel Griesbeck, Joachim Mattay, Hana Griesbeck and Heinz Roth. Budapest, 2002. Private collection SEB

Miguel Angel Miranda (Figure 48) was the Chair of the twentieth IUPAC Symposium on Photochemistry held in Granada. *Bartolomé Quintero* (Figure 49) led the local Organizing Committee.

Figure 48. From left: Jeanne Weiss, Miguel A. Miranda, Miguel Neumann and Dick Weiss. Granada, 2004. Private collection SEB

Figure 49. From left: Amalia Miranda (sitting), Tito Scaiano and wife Elda, Ana Moore and Bartolomé Quintero. Granada, 2004. Private collection, SEB.

Table 21. XXth IUPAC Symposium on Photochemistry – Granada – Spain, 2004. Papers published in [50].

H. M. Vaswani, N. E. Holt and G. R. Fleming, Carotenoid-chlorophyll complexes: Ready-to-harvest

J. Cadet, Sophie Courdavault, J.-L. Ravanat and T. Douki, UVB and UVA radiation-mediated damage to isolated and cellular DNA

K. Kawai and T. Majima, Photosensitized one-electron oxidation of DNA

A. Sinicropi, T. Andruniow, L. De Vico, N. Ferré and M. Olivucci, Toward a computational photobiology

V. Lhiaubet-Vallet, Photosensitization by chiral drugs: Looking for stereodifferentiating photoprocesses in the presence of biomolecules

R. E. Palacios, S. L. Gould, C. Herrero, M. Hambourger, A. Brune, G. Kodis, P. A. Liddell, J. Kennis, A. N. Macpherson, D. Gust, T. A. Moore and A. L. Moore, Bioinspired energy conversion

J. C. Scaiano, C. Aliaga, M. N. Chrétien, M. Frenette, K. S. Focsaneanu and L. Mikelsons,
Fluorescence sensor applications as detectors for DNA damage, free radical formation, and in microlithography

H. Inoue, S. Funyu, Y. Shimada and S. Takagi, Artificial photosynthesis via two-electron conversion: Photochemical oxygenation sensitized by ruthenium porphyrins with water as both electron and oxygen atom donor

A. D'Aléo, S. Welter, E. Cecchetto and L. De Cola, Electronic energy transfer in dinuclear metal complexes containing *meta*-substituted phenylene units

A. Credi and B. Ferrer, Rotaxane-based molecular machines operated by photoinduced electron transfer

A. G. Griesbeck, T. T. El-Idreesy and A. Bartoschek, Photooxygenation in polymer matrices: *En route* to highly active antimalarial peroxides

H. D. Roth, Return electron transfer in radical ion pairs of triplet multiplicity

Graham Fleming (Figure 50) received the Porter Medal. In his lecture he showed how a combination of advanced time-resolved techniques (in transient absorption and emission) and computations provide an insight into the mechanisms underlying the rapid processes of energy transfer in the antennas of the photosynthetic units. *John Polanyi* (Chemistry Nobel Laureate in 1986) gave a Plenary Lecture on "Reaction dynamics a molecule at a time: Patterns of photochemical reaction at Silicon studied by scanning tunneling microscopy". Three parallel sessions focused on the various aspects of photochemistry. *X. Sunney Xie* presented a talk on "Single molecule studies of electron transfer in biological systems" showing data of transfer from a donor tyrosine to an acceptor flavin in the enzyme flavin oxidoreductase. *Ana Moore* took the audience through a tour of the several years of efforts to realize man-made bioinspired photosynthesis. *Haruo Inoue* also showed the advances in their efforts in the area of man-made photosynthesis. These talks and several other contributions showed that many groups were making progresses in the direction of biomimetic energy conversion. *Massimo Olivucci* elaborated on the impressive advances of the calculations of trajectories after excitation of chromoproteins. *Paul Barbara* described methods to measure charge mobility in photoconducting polymers at the level of single molecule. There was no report of this Symposium in the *EPA Newsletters*, since *Jean Kossanyi* (Figure 10), editor at the time of the *EPA Newsletter*, had passed away in 2004 [51] and it took some time to resume the regular publication of the *EPA Newsletters*. A report of the Symposium was published in the Newsletters of the I-APS [52].

Figure 50. Graham Fleming

The twenty-first IUPAC Symposium on Photochemistry was taken by its scientific Chairman *Masahiro Irie* (Figure 51) to Kyoto in April 2006 during the Cherry Blossom season (a wonderful time of the year!). The previous symposia (all in Europe) had been in general at the end of July. Chairman of the local Organizing Committee was *Atsuhiro Osuka* (Figure 52).

Figure 51. Masahiro Irie

Figure 52. Atsuhiro Osuka.

Table 22. XXIst IUPAC Symposium on Photochemistry – Kyoto – Japan, 2006. List of papers published in [53].

H. E. Zimmerman (Porter Medal), Five decades of mechanistic and exploratory organic photochemistry

H. Masuhara (Porter Medal), T. Asahi and Y. Hosokawa, Laser nanochemistry

C. Schäfer, B. Decker, M. Letzel, F. Novara, R. Eckel, R. Ros, D. Anselmetti and J. Mattay, On the way to supramolecular photochemistry at the single-molecule level

J. Hofkens, T. D. M. Bell, A. Stefan, E. Fron, K. Müllen and F. C. De Schryver, Probing molecular properties and the role of the environment at the single-molecule level

K. Maeda, K. Teramura, N. Saito, Y. Inoue, H. Kobayashi and K. Domen, Overall water splitting using (oxy)nitride photocatalysts

V. Lhiaubet-Vallet and M. A. Miranda, Drug-biomolecule interactions in the excited states

F. D. Lewis, DNA photonics

S. Kanvah and G. B. Schuster, Oxidative damage to DNA: Inhibition of guanine damage

J.-P. Desvergne, A. G. L. Olive, N. M. Sangeetha, J. Reichwagen, H. Hopf and A. Del Guerzo. Self-assembling and light-harvesting properties of fluorescent linear condensed aromatic gelators

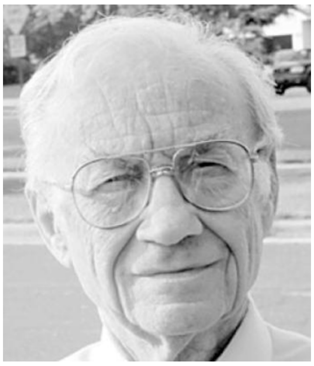

Figure 53. Howard Zimmerman

Howard Zimmerman (Figure 53) [54] and *Hiroshi Masuhara* (Figure 54) [55] received each a Porter Medal for their life work. The

Symposium was very well attended with 777 participants. Parallel sessions with a total of 278 presentations were organized. A total of 450 posters were presented.

Figure 54. Hiroshi Masuhara

William E. Moerner (Chemistry Nobel Prize in 2014) held the opening plenary lecture with the title "Single Molecules as Nanoscale Reporters in Biophysics, Chemistry, and Material Sciences". *Klaus Müllen* introduced the new family of synthetic dyes derived from the commercial perylenetetracarboxydiimide, with optical, morphological and other properties, suitable for very different applications. Some of the studies with these molecules were explained by *Frans De Schryver* in his talk "Probing molecular properties and the role of the environment at the single-molecule level". *Mireille Blanchard-Desce* talked about "Molecular engineering of two-photon absorbing molecules for bioimaging". All these contributions show a high level of multidisciplinary collaboration. *Paul Corkum* offered a talk with the title: "Attosecond imaging: Asking a molecule to paint a self-portrait" and *Lei Jiang* talked about "UV-manipulated switch between superhydrophobicity and superhydrophilicity". *Niek F. van Hulst* gave a talk about "Ultrafast femtosecond single molecule spectroscopy" and *Monique Martin* demonstrated that charge transfer is the driving force for the photoactivity of the PYP chromophore in solution. There were several presentations and many posters in the area of photobiology. *Masahide Terazima* showed the power of photorefractive techniques in his talk on "Time-resolved studies of conformational changes of photo-response proteins in solution" and his group presented 5 posters with applications of the technique to various chromoproteins. *Jacques Moser* (with co-authors *Bernard Wenger* and *Michael Grätzel*) presented the initial talk in a Workshop on solar cells: "Dynamics of light-induced interfacial electron transfer in the dye-sensitization of nanocrystalline oxide semiconductors".

During the workshop on solar cells *Josef Michl* was one of the scheduled speakers with the lecture: "Search for singlet-fission sensitizers for a more efficient solar cell". In view of the technical difficulties to connect *Josef*'s laptop, he decided to give the talk without slides. We could really follow the wonderful explanations with no figures. Notwithstanding this, *Josef* was given the opportunity later during the Symposium to repeat his presentation, in this case with connected laptop!

Figure 55. Heinz Roth singing at the Banquet in Kyoto (April 2006)

One of the main goals of many research groups in photochemistry is obtaining long-lived charge-separated states capable of sustaining an electron transfer chain for solar energy conversion. In search of this goal, *Sunishi Fukuzumi* reported during his talk the finding of a long-lived charge-separated state photoproduced in newly synthesized dyads containing the acridinium ion. In the same session, *Jan Verhoeven*, in his invited presentation, challenged *Fukuzumi's* interpretation of the data arguing that the long-lived states corresponded to the well known triplet states of the acridinium ion. A lively discussion followed the presentations.

Figure 56. Franco Scandola with a Geisha during the banquet, Kyoto, 2006

Figure 57. Hermenegildo García and Enrique San Román with a Geisha

Figure 58. From left: Klaas Zachariasse, Masahide Terazima, and Gabriel Andrés with Cherry trees

During the banquet *Heinz Roth* entertained us with some beautiful singing (Figure 55). Figures 56 - 58 show various colleagues during the Symposium Banquet and with the Cherry trees. There was no published report on this Symposium.

Figure 59. Devens Gust

The twenty-second IUPAC Symposium was chaired by *Devens Gust* (Figure 59) and held in Göteborg in 2008. The local Organizing Committee was chaired by *Bo Albinsson* (Figure 60).

Figure 60. Bo Albinsson

Table 23. XXIInd IUPAC Symposium on Photochemistry – Göteborg – Sweden, 2008. List of papers published in [56].

J. M. G. Martinho, T. J. V. Prazeres, L. Moura and J. P. S. Farinha, Fluorescence of oligonucleotides adsorbed onto the thermoresponsive poly(isopropyl acrylamide) shell of polymer nanoparticles: Application to bioassays

D. Markovitsi, Interaction of UV radiation with DNA helices

D. Vobornik, D. S. Banks, Z. Lu, C. Fradin, R. Taylor and L. J. Johnston, Near-field optical probes provide subdiffraction-limited excitation areas for fluorescence correlation spectroscopy on membranes

M. Irie and M. Morimoto, Photochromic diarylethene molecules and crystals

J. A. Calladine, K. Q. Vuong, X. Z. Sun and M. W. George, Recent advances in organometallic alkane and noble gas complexes

V. Darcos, C.-H. Huang, N. McClenaghan, Y. Molard, J. H. R. Tucker, Y. Vida Pol, E. Pérez-Inestrosa and D. M. Bassani, Shining light on supramolecular assemblies

F. H. Quina, P. F. Moreira, Jr., C. Vautier-Giongo, D. Rettori, R. F. Rodrigues, A. A. Freitas, P. F. Silva and A. L. Maçanita, Photochemistry of anthocyanins and their biological role in plant tissues

I. González-Ramírez, T. Climent, J. J. Serrano-Pérez, R. González-Luque, M. Merchán and L. Serrano-Andrés, The role of pyrimidine nucleobase excimers in DNA photophysics and photoreactivity

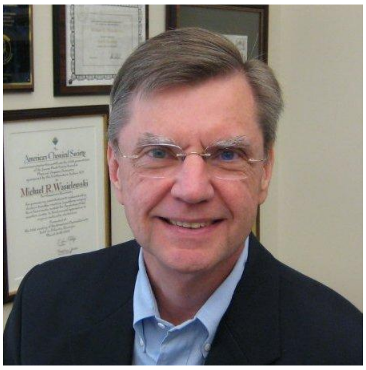

Figure 61. Michael Wasielewski

The opening Plenary Lecture was delivered by *Eric Vauthey* on "Photoinduced electron transfer reactions: From basic questions to potential applications". *Michael Wasielewski* (Figure 61) received the Porter Medal and gave a lecture on "Charge and spin dynamics in molecules and materials: from photosynthesis to spintronics". The EPA conferred for the first time a prize to a young investigator (together with the Journal *PPS*) and one for the best PhD Thesis in Photochemistry. The awardees were *Alexandre Fürstenberg* (Geneva) and *Maria Abrahamsson* (Uppsala), respectively, each of whom delivered a lecture after receiving the award. *Stefan Hell* (Chemistry Nobel Prize in 2014) gave a lecture on "Far-field fluorescence nanoscopy", sponsored by the Journal *Photochemical and Photobiological Sciences*. *Harry Gray* delivered a lecture on "Electron tunneling through proteins" and *Vincenzo Balzani* one on "Molecular devices and machines". Many groups showed the progress on solar energy conversion in its various approaches, such as new types of solar cells, photocatalytic hydrogen formation, nanostructured electrodes, and others. *Leif Hammarström* offered a talk on "Biomimetic approaches to artificial photosynthesis. Controlling coupled electron transfer". In the three parallel sessions contributions on single molecule spectroscopy as well as on nanodevices, analytical devices using fluorescence as well as on molecular aspects of photobiological processes and organic photochemistry were presented. Major progresses in calculations of excited species were shown. *Josef Michl* demonstrated that new ways of solar energy conversion may be possible in his talk "Singlet fission – can it be harnessed?". The Bordeaux group (*Dario Bassani et al.)* demonstrated an important progress in the collaborative work on supramolecular structures. There were 430 participants from 51 Countries. A report on the Symposium was published in [57].

Figure 62. Franco Scandola

Figure 63. David Phillips

The twenty-third IUPAC Symposium was chaired by *Franco Scandola* (Figure 62) in Ferrara in 2010, with the help of *C. Chiorboli* as head of the local organizing Committee.

Table 24. XXIIIrd IUPAC Symposium on Photochemistry – Ferrara – Italy, 2010. List of papers published in [58].

D. Phillips (Porter Medal), Toward targeted photodynamic therapy

W. Song, Z. Chen, M. Kyle Brennaman, J. J. Concepcion, A. O. T. Patrocinio, N. Y. Murakami Iha and T. J. Meyer, Making solar fuels by artificial photosynthesis

W. Liang, H.-H. Zhang, J.-J. Wang, Y. Peng, B. Chen, C. Yang, C.-H. Tung, L.-Z. Wu, G. Fukuhara, T. Mori and Y. Inoue, Supramolecular complexation and photocyclodimerization of methyl 3-methoxy-2-naphthoate with modified γ-cyclodextrins

S. Ramachandra, F. Polo, F. Edafe, K. C. Schuermann, C. A. Nijhuis, Pe. Belser, W. F. Reus, G. M. Whitesides and L. De Cola, Luminescent acetylthiol derivative tripodal osmium(II) and iridium(III) complexes: Spectroscopy in solution and on surfaces

E. Oliveros, M. L. Dántola, M. Vignoni, A. H. Thomas and C. Lorente, Production and quenching of reactive oxygen species by pterin derivatives, an intriguing class of biomolecules

A. Kotiaho, R. Lahtinen and H. Lemmetyinen, Photoinduced processes in chromophore–gold nanoparticle assemblies

K. Kam-Wing Lo, K. Yin Zhang and S. Po-Yam Li, Design of cyclometalated iridium(III) polypyridine complexes as luminescent biological labels and probes

J. Narasimha Moorthy, S. Samanta, A. L. Koner and W. M. Nau, Steady-state photochemistry (Pschorr cyclization) and nanosecond transient absorption spectroscopy of *twisted* 2-bromoaryl ketones

Y. Zhang, E. Galoppini, P. G. Johansson and G. J. Meyer, Homoleptic star-shaped Ru(II) complexes

H. Masuhara, T. Sugiyama, T. Rungsimanon, K.-i. Yuyama, A. Miura and J.-R. Tu, Laser-trapping assembling dynamics of molecules and proteins at surface and interface

R. Toftegaard, J. Arnbjerg, H. Cong, H. Agheli, D. S. Sutherland and P. R. Ogilby, Metal nanoparticle-enhanced radiative transitions: Giving singlet oxygen emission a boost

K. Yoosaf, A. Belbakra, A. Llanes-Pallas, D. Bonifazi and N. Armaroli, Engineering supramolecular photoactive nanomaterials by hydrogen-bonding interactions

J. C. Scaiano, J. C. Netto-Ferreira, E. Alarcon, P. Billone, C. J. Bueno Alejo, C.-O. L. Crites, M. Decan, C. Fasciani, M. González-Béjar, G. Hallett-Tapley, M. Grenier, K. L. McGilvray, N. L. Pacioni, A. Pardoe, L. René-Boisneuf, R. Schwartz-Narbonne, M. J. Silvero, K. G. Stamplecoskie and T.-L. Wee, Tuning plasmon transitions and their applications in organic photochemistry

David Phillips (Figure 63) was awarded the Porter Medal [59]. The opening Plenary Lecture was given by *Tom Meyer* on "Making solar fuels at interfaces", followed by an Invited Lecture by *Paul Barbara* on "Sub-nanometer optical single molecule experiments on charge separation and trapping in conjugated polymers". It was the last time the photochemical community enjoyed his brilliant lectures, since *Paul* passed away some months after the Symposium. Again in this Symposium there was a large number of presentations showing the various efforts to understand the natural photosynthetic processes and to develop better systems for solar energy conversion. In addition to the talk by *Tom Meyer*, *Rink van Grondelle* explained how using ultra-short time spectroscopies his group has found that "Conformational switching in plant light harvesting complexes regulates photosynthesis", from efficient energy transfer under low intensity light to heat dissipation under elevated radiation conditions.

Figure 64. Hugh Burrows

Daniel Nocera focussed his talk on the possibility of solar energy storage through a two-electron reductive elimination of halogen from a metal center. *Massimo Olivucci* showed how, based on their advanced computational studies, it is possible to start designing (and synthesizing) molecules mimicking the photoisomerization of retinal-proteins. *Stefan Matile* described the strategy to build "Supramolecular architectures for artificial photosynthesis" and *Devens Gust* explained how it is possible "Controlling light by light: From photosynthesis to molecule-based signal transduction". The EPA-*PPS* prize was conferred to *Werner Nau*, whereas the prize for the best thesis in photochemistry was given to *Anne Kortiaho* (Tampere, Finland) [60].

The twenty-fouth IUPAC Symposium on Photochemistry was held in Coimbra, Portugal, in 2012. Scientific Chair was *Hugh Burrows* (Figure 64) and head of the Organizing Committee was *Artur J. M. Valente* (Figure 65).

Figure 65. Artur J. M. Valente

Table 25. XXIVth IUPAC Symposium on Photochemistry – Coimbra – Portugal, 2012. List of papers published in [61].

D. W. Thompson, A. Ito and T. J. Meyer (Porter Medal)
$[Ru(bpy)_3]^{2+*}$ and other remarkable metal-to-ligand charge transfer (MLCT) excited states
J. M. Anna, Y. Song, R. Dinshaw and G. D. Scholes, Two-dimensional electronic spectroscopy for mapping molecular photophysics
V. Wing-Wah Yam, Photofunctional organometallics - from fundamentals to design, assembly and functions
I. V. Sazanovich, M. A. H. Alamiry, An. J. H. M. Meijer, M. Towrie, E. S. Davies, R. D. Bennett and J. A. Weinstein, Photoinduced charge separation in a Pt^{II} acetylide donor–acceptor triad based on 2-(1-pyrazole)-pyridine modified with naphthalene mono-imide electron acceptor
M. A. H. Alamiry, E. Bahaidarah, A. Harriman, J.-H. Olivier and R. Ziessel, Influence of applied pressure on the probability of electronic energy transfer across a molecular dyad

M. Fujitsuka and T. Majima, Charge transfer in DNA
F. D. Lewis and M. R. Wasielewski, Dynamics and efficiency of photoinduced charge transport in DNA: Toward the elusive molecular wire
L. G. Arnaut and S. J. Formosinho, From elementary reactions to chemical relevance in the photodynamic therapy of cancer
S. Yu, Feng Wang, J.-J. Wang, H.-Y. Wang, B. Chen, K. Feng, C.-H. Tung and L.-Z. Wu, Light-driven hydrogen evolution system with glutamic-acid-modified zinc porphyrin as photosensitizer and [FeFe]-hydrogenase model as catalyst
Y. Hisaeda, K. Tahara, H. Shimakoshi and T. Masuko, Bioinspired catalytic reactions with vitamin B_{12} derivative and photosensitizers
Nobuhiro Ohta, Electric-field effects on photoinduced dynamics and function
M. Canle López, M. I. Fernández, C. Martínez and J. A. Santaballa, Photochemistry for pollution abatement
K. Santhosh, G. Krishnamurthy Grandhi, S. Ghosh and A. Samanta, A fluorescence study of the solute–solvent interactions of aminochalcones in a room-temperature ionic liquid
G. Yang, S. Li, S. Wang, R. Hu, J. Feng, Y. Li and Y. Qian,
Novel fluorescent probes based on intramolecular charge- and proton-transfer compounds
S. Protti, D. Ravelli, M. Fagnoni and A. Albini, Smooth photogeneration of α,*n*-didehydrotoluenes (DHTs)
C. F. Sailer and E. Riedle, Photogeneration and reactions of benzhydryl cations and radicals: A complex sequence of mechanisms from femtoseconds to microseconds
S. Arumugam, S. V. Orski, N. Eric Mbua, C. McNitt, G.-J. Boons, J. Locklin and V. V. Popik, Photo-click chemistry strategies for spatiotemporal control of metal-free ligation, labeling, and surface derivatization

Tom Meyer received the Porter Medal (Figure 66) [62]. The Symposium opened with Plenary lecture by *Gregory Scholes* on "Quantum mechanisms for light harvesting in photosynthesis" followed by three parallel sessions with Invited Lectures and later on with oral communications. There were 600 participants and a very wide repertoire of subjects. A novel aspect was presented in the talk by *Maria João Melo* about "Photochemistry of cultural heritage". The talk by *Tetsuro Majima* treated the hole transport in DNA and *Guillermo Bazán* described the use of poly- and oligo-electrolytes in optoelectronics and bioelectronics. *Anthony (Tony) Harriman* and *Franco Scandola* (the latter in a lecture sponsored by the journal *PPS*) described strategies for the production of synthetic harvesting antennas and artificial photosynthetic units, respectively, whereas *Ben Feringa* reported the latest advances regarding the "Design, synthesis and functioning of molecular systems with optical molecular switches and light-driven molecular motors". The extended sessions on solar energy conversion devices, photovoltaic cells, and other improvements in this direction were very well attended. Several Invited Lectures were given by Chinese photochemists, underscoring the Chinese modern scientific development, and of course several Invited Lectures were from Japanese and South Korean colleagues. *Sebastião Formosinho* shared his talk with *Luis Arnaut* about "Rational design of photodynamic photosensitizers". Ultrafast absorption and emission techniques, single molecule detection, cross-correlation emission, nanotechnologies, and micro- and nano-scopies have become regular techniques in several laboratories around the world. Reports about the use of these techniques were presented in oral communications and posters.

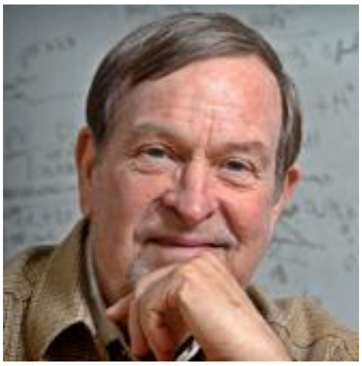

Figure 66. Tom Meyer

The EPA prize for the best thesis in photochemistry 2011-2012 was awarded to *Karl Börjesson* (Chalmers University). *Mike Heilemann* was the recipient of the EPA-*Photochemical and Photobiological Sciences* (*PPS*) Prize Lecture [63]. The Langmuir award for best presentation in the Young Photochemists' session was given to *Danielle Wilson* (Victoria University, Canada) and special commendations were given to *Laurence Pessoni* (Université de Pau et des pays de l'Ardour, France) and to *Marina Blanco-Lomas* (Universidad de La Rioja, Spain).

Figure 67. Dario Bassani

Figure 68. Andre del Guerzo

The twenty fifth IUPAC Symposium on Photochemistry was held in Bordeaux in 2014. Scientific Chairman was *Dario Bassani* (Figure 67) and local Co-Chair organizers were *André del Guerzo* (Figure 68) and *Nathan McClenaghan* (Figure 69). The Symposium marked the 50 years of IUPAC Photochemistry, a proud anniversary celebration with 631 participants from 41 Countries.

Table 26. XXVth IUPAC Symposium on Photochemistry – Bordeaux – France, 2014. List of Plenary and Invited Lectures.

M. Irie (Porter Medal) Making and breaking bonds with light: Discovery and development of photochromic diaryethenes
J. Abe, Fundamentals and applications of fast photochromic materials
Ja. McCusker, Spin effects on energy and electron transfer processes
C. Adachi, Molecular design for high efficiency delayed fluorescence and their application in organic light emitting diodes
U. Pischel, Photochromic switches for advanced molecular information processes
M. García Garibay, Reaction yield amplification by quantum-chain photochemical reactions in crystalline solids
M. Fujita, Trapping reaction intermediates photochemically generated in a synthetic cavity
A. Ajayaghosh, Photoresponsive supramolecular assemblies and gels
V. Plyusnin, Photochemistry and photochemistry of the dithiolate Cu(III) and Ni(III) complexes. Processes from hundreds of femtoseconds to seconds
O. Wolfbeis, Chemical sensing and biosensing using advanced fluorescent (nano) materials
H. Misawa, Plasmon-assisted artificial photosynthesis systems
C. Turro, Excited states of inorganic complexes for applications in biology and sustainable energy
A. Credi, The ethernal youth of azobenzene: New photoactive molecular and supramolecular devices and materials
D. Leigh, Making the tiniest machines
C. Timmel, "A bird's eye view" of cavity-based absorption spectroscopy of radical pairs
F. Odobel, Molecular systems to mimic the charge photoaccumulation and the Z scheme functions of biological photosynthesis
A. Griesbeck, Singlet oxygen reactions: new selectivity modes and synthetic applications
L. Flamigni, Functional arrays for light energy capture and charge separation
M. Chergui, Ultrafast relaxation dynamics in metal complexes: interplay of spin, electronic and structural rearrangements
L. Tolbert, Turn-on fluorescent sensors for biological applications
H. Uji-i, Sub-diffraction limited remote excitation of surface enhanced Raman/fluorescence spectroscopy
J. Zhao, Selective organic synthesis mediated by TiO_2 photocatalysis
> *M. Kuimova*, Mapping microscopic viscosity with molecular rotors: from live cells to atmospheric aerosols
J. Andreasson, Photochromic control of DNA-binding with added value
W. Skene, Autochromes: reversible polymers for fluorescence tuning

J.-M. Lehn, Towars adaptive chemistry. Aspects of photoinduced processes
S. E. Braslavsky, The history of the IUPAC Symposia on Photochemistry – a success story
H. Burrows, Uranyl ion photochemistry revisited
N. Hoffmann, Photochemically induced radical reactions with furanones
G. La Ganga, Artificial photosynthesis: a molecular approach to photoinduced water oxidation
M. Litter, Mechanisms of removal of heavy metals and arsenic from water by TiO_2-heterogeneous photocatalysis

Figure 69. Nathan McClenaghan

The Porter Medal was awarded to *Masahiro Irie* (see Figure 51) for his work on photochromic materials. In his talk he offered a historical view about the development of these materials, including the strong scientific contacts with colleagues from Bordeaux, and even performed an experiment on photochromism. *David Leigh* elaborated on "Making the tiniest machines" and, by the way, performed several very entertaining magic tricks during his lecture! The opening Plenary Lecture was given by *Jiro Abe* on "Fundamentals and applications of fast photochromic materials". *Miguel García Garibay* delivered a talk on "Reaction yield amplification by quantum-chain photochemical reactions in crystalline solids".

There were three parallel sessions. Several talks were presented on the use of scaffolds for the production of man-made photosynthetic systems, such as those developed in *Bo Albinson's* lab using self-assembled DNA nanosystems for energy and electron transfer applications. *Lucia Flamigni* spoke also on "Functional arrays for light energy capture and charge separation". "Chemical sensing and biosensing using advanced fluorescent (nano) materials" was the title of the talk given by *Otto Wolfbeis*. Many talks were devoted to progress in luminescent sensors for biological applications, such as those by *Laren Tolbert* and by *Willi Skene*. *Jean-Marie Lehn* (Chemistry Nobel Laureate in 1987) developed his ideas "Towards adaptive chemistry. Aspects of photo-induced processes". *Hugh Burrows* in his talk revisited the photochemistry of the uranyl ion. The International Foundation of Photochemistry sponsored the lecture by *Marta Litter* in which she explained why photocatalysis is the method of choice to remediate waters contaminated with metal ions.

The EPA-*PPS* Prize Lecture was delivered by *Norbert Hoffmann* and the EPA PhD Prize lecture was given by *Giuseppina La Ganga* (Univ. Messina). There were also Poster Award presentations.

This account is a mere progress report of the successful story of the IUPAC Symposia on Photochemistry. The series will hopefully continue with prominent actors, very engaged young students and researchers, interesting results, and a large number of successful international projects. The Symposia have given strong impulses to the field. The theoretical and practical knowledge gained over these 50 years of IUPAC Photochemistry has been enormous. Many of the applications developed have undoubtely contributed to a better life for our societies. In the UNESCO Year of light (2015) [63], the photochemical community is proud to be a highly interdisciplinary group of colleagues actively collaborating with each other, working with light and developing tools using light, with a large number of students following the steps of many brilliant scientists that have enlightened the path over many years.

Acknowledgments. "With a little help from my friends": Dario Bassani, André Braun, Dietrich Döpp, Devens Gust, Helmut Görner, Fred Lewis, Kurt Schaffner, Joggi Wirz. I deeply thank them all for their great help and critical reading of the ms.

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

A guided tour of the laboratories across the "Régions"

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Part I

The first steps

Textbooks are rather silent about the early stages of the history of photochemistry (Roth, 2001a). In France, an important event was the discovery of photography in 1822 by *Nicéphore Niépce*, who observed that bitumen of Judea (asphalt) solidifies and becomes insoluble under light irradiation (Marignier, 1994). In 1839, *Jacques Daguerre* improved the technique and, in 1891, *Gabriel Lipmann* discovered the first direct process for colour photography (Marignier, 1994). *Edmond Becquerel* became famous for the photovoltaic effect observation (1939) that was called "Becquerel effect" (Becquerel, 1839). He also invented the phosphoroscope equiped with a rotating disc to determine the phosphorescence lifetime (exposed in the Conservatoire des Arts et Métiers (CNAM) museum, in Paris). *Jean Perrin's* laboratory, in Paris, then led by his son *Francis*, was, in the beginning of the XXth century, a high spot for the international elite of physicists (Perrin, 1929). It is in this intellectual bath that *Victor Henri* studied spectroscopy and demonstrated that predissociation is at the origin of the widening the rotovibronic bands of the electronic spectra of small molecules in the gas phase. He also discovered photochemical chain reactions (Henri and Teves, 1924). Father and son *Perrin* provided, in 1929, an interpretation for the thermally activated delayed fluorescence (so-called "E"), that involves a metastable state as an intermediate, identified later by others as the triplet state. They also made a *major contribution* to the establishment of the famous *Jablonski-Perrin diagram* (Nickel, 1996), now used by all photochemists. Although it is not directly related to photochemistry, the pioneering work of *Paul Job* for his spectroscopic method to determine the stoichiometry of molecular complexes is still very much used to-day (Job, 1928).

The first results in organic photochemistry were obtained in Germany by J. Fritzsche (Fritszche, 1867) and H. Klinger (Klinger,1886), in Italy by Giacomo Ciamician, considered as the father of organic photochemistry (Ciamician & Silber, 1886, 1900, 1909; Ciamician, 1912) as well as Emanuele Paternò (Paternò & Chieffi, 1909; see also Roth, 1988, 1989, 2001a, 2001b; Albini, 2008) and in Egypt by Alexander Schönberg (Schönberg, 1958). The first publications in France were the works of *Daniel Berthelot* on the photolysis of acetone (Berthelot & Gaudechon, 1910) and of *Guy Emschwiller* who investigated the photolysis of alkyl iodide in 1924 (Job & Emschwiller, 1924) and 1930 (Emschwiller, 1930) as well as that of potassium ferrocyanide in aqueous solution (Emschwiller & Legros, 1954). At that time, *Charles Dufraisse* became famous through the study of photooxygenation of naphthacenes and anthracenes showing the "labile union" of oxygen with carbon (Dufraisse, 1936).

The laboratory of physical chemistry, founded by *Jean Perrin* in 1930 in Paris, was led in 1945 by Edmond Bauer. It is there that *Michel Magat* started the study of organic molecules under radiation (Magat, 1971) and *Sydney Leach* applied molecular spectroscopy to the detection and characterization of transients trapped at low temperature. Then *Magat* and *Leach* moved towards the new buildings of Orsay (*vide infra*).

Despite these remarkable accomplishments, photochemistry did not show a large development in France, whereas it was expanding in the USA. Therefore, some French PhDs made postdoctoral stays in well-known American groups such as those of George Hammond, Albert Noyes, Howard Zimmerman, Gerald Oster, Paul de Mayo, etc. On their return, they founded several laboratories centered on photochemical transformations.

Expansion of Research in France (from the 1960s)

The French Group of Photochemistry

A milestone was set on November 3, 1967, when *Jean Rigaudy* and *Pierre Courtot* called all French resarchers having an activity in photochemistry and photophysics to meet at the "Ecole Supérieure de Physique et Chimie Industrielle, Paris (ESPCI) " (Table A,a). The group, that later became the French Photochemistry Group, met for the first time on February 9, 1968. The meetings (two per year) were successfully run by *Courtot* from 1968 to 1985, then *Roland Bonneau* took over the chairmanship (1985-1993), organizing, *inter alia*, a Franco-Italian colloquium in 1989 (Table E,l). He was followed by *Jean Kossanyi* (1993-1999), *Robert Pansu* (1999-2002), *Thu-Hoa Tran Thi* (2002-2005) and *Edmond Amouyal* from 2007 (*Mohamed Sarakha*, vice-president).

The group, recognized by the French Chemical Society as "thematic group", changed its name in 2008 into " Goupe Français de Photochimie, Photophysique et Photosciences (GFP2P) (Table A,a). Along the years, the bi-annual meetings gather about 40 participants for a joint meeting with the SFPb, *vide infra*.

French Society for Photobiology (SFPb)

In 1929, the state-approved "Société Française d'Actinologie", was composed of researchers from several disciplines (physicists, biologists, chemists...). The group, which later became the French Society for Photobiology, meets at least once a year. The present executive committee includes *Evelyne Sage* (president), *Christine Vever-Bizet* (treasurer) and *Thierry Douki* (secretary). The association organized in Paris (June 2015) a colloquium on the photoprotection, where *Jean-François Doré* (Institut National de la Santé et de la Recherche Médicale: INSERM, Lyon) specialist of skin cancer, gave a talk (see Green *et al.*, 2006). In parallel, it is appropriate to mention the Society of photodermatology, founded in 1990 named "Société Française de PhotoDermatologie (SFPD)" whose "17th national meeting" (so-called national days) occurred in Angers (March 2015).

A joint meeting of the GPP2P and the GFPb, coorganized by their respective presidents, *Edmond Amouyal* and *Evelyne Sage*, entitled "Lumière sur la Photochimie et la Photobiologie" was held on December 8-9, 2015 at Cachan.

European Associations

European Photochemistry Association (EPA)

The "European Photochemistry Association" (EPA) was set up in 1970, under the auspices of the Council of Europe in order to develop experimental and theoretical aspects of interaction of light with matter: photochemistry at large, including photophysics, photography, spectroscopy, radiation chemistry... with applications to electronics, materials science, biology and medicine. The objective of the association was to organize common meetings, Summer schools, exchanges of researchers, a common journal and other means of cooperation (Table A, b). Among the midwives of the birth of EPA, the French delegation was composed of *Pierre Courtot* and *Jacques Joussot-Dubien.* The first formal meeting took place in Bordeaux, on the occasion of the "Vth International Conference on Photochemistry", in 1971 (Table E,d). Soon thereafter (1983), the EPA had about 950 members from 40 different countries.
The French participants to the executive committee were:
Presidents: *Jacques Joussot-Dubien* (1976-1980); *Dimitra Markovitsi* (2007-2010); Vice-president: *Jean-Pierre Pete* (1996-2000); secretaries: *Jean Kossanyi* (1972-1976), *Henri Bouas-Laurent* (1984-1986), *Elisabeth Poquet* (1988-1990), *Eva Migirdicyan* (1990-1994). Many other French members served on national committees. *Joussot-Dubien* managed to launch the "EPA Newsletter" (EPA NL). The first issues were printed at the Max Planck Institute in Mülheim a. d. Ruhr, in 1978, under the guidance of Hans-Jochen Kuhn, as co-editor with S. G. Boué (Bruxelles). Kuhn became later Managing Editor (1990-1999) prior to *Jean Kossanyi* (1999-2004), followed by *Mohamed Sarakha* (2004-2005) and *Dimitra Markovitsi* (2006-2007). Then others took up the responsibility. Now, the EPA NL is published in electronic and printed form. A comprehensive report on the activity of the French laboratories was written in 1981 by *Migirdicyan* and *Pete* (Migirdicyan & Pete, 1981). In 2001, EPA and ESP (European Society for photobiology, *vide infra*) agreed to found a common journal: "Photochemical & Photobiological Sciences" (PPS), published by the Royal Society of Chemistry. The is co-owned by the EPA and ESP, and the "Asia & Oceania Society for Photobiology" and "Korean Society of Photoscience" are affiliated to the journal. The well documented history of the EPA up to 2012 was described by Ugo Mazzucato (Mazzucato, 2012 and 2013).

The general assembly takes place every other year on the occasion of the "IUPAC Symposium" (*vide infra*).

European Society for Photobiology (ESP)

ESP was founded in 1985 by Giulio Jori, a pioneer of photodynamic therapy (deceased in 2014). A conference is organized every other year. The 16th ESP Congress was held at Aveiro (Portugal) in 2015 where *Serge Mordon* (Lille) and *Virgile Adam* (Grenoble) were lecturers. Schools are also set up. "Photodynamic therapy" is a regular topic for an international symposium; the 10th edition occurred at Brixen (Bessanone, Italy) in 2014. The 11th one is scheduled to be organized by *Cécile Frochot* in Nancy (France) in 2016.

International Conferences

The main international meetings on photochemistry were born after 1960.

The oldest one, called "Informal Conference on Photochemistry" was founded by Francis E. Blacet (UCLA) in 1962 and was held in Northern America every two years up to 2000, and then at San Juan in Porto Rico.

A second conference was initiated at North Carolina University by George Wyman (April 16-18, 1962). Wyman was then director of the chemistry division in the research department of the American Army. The number of delegates was limited to 125, on invitation. The only French researcher was *Lars Lindqvist* (*vide* Orsay). This symposium was later named "International Conference on Photochemistry" (ICP). It now takes place every two years (alternatively with the IUPAC Symposium, *vide infra*) in different places worldwide (USA, Japan, Europe, Israël, China...). Two of them were organized in France, the Vth (1971) in Bordeaux and the XVth in Paris (1991) (Table E,d,e). The talks presented in 1962 were printed in the "Journal of Physical Chemistry" (Wyman, 1999). The XXIIth ICP was held in Korea (Jeju Island) in July 2015.

Another series of conferences, sponsored by the International Union of Pure and Applied Chemistry (IUPAC) started in Strasbourg in 1964, organized by George Hammond (Chairman) and *Jacques Levisalles* (local organizer). The first meeting was called "Symposium on Organic Photochemistry". Very rapidly, it was extended to other areas of photochemistry and was renamed "IUPAC Symposium on Photochemistry", taking place alternatively with the ICP. In addition of that of Strasbourg, three other Symposia were held in France (Table E, a,b,c), particularly in Bordeaux for the 50th anniversary of the series (chairman: *Dario Bassani*, 2014). It was an adequate forum for Silvia Braslavski to give a bright lecture about the history of these symposia (Braslavski, 2014 and 2015). The symposia occur generally in Europe, exceptions being 2006 (Kyoto, Japan) and 2016 (Osaka, Japan).

Other conferences or associations

The "Gordon Conference on Photochemistry" started in 1964 at Tilton (New Hampshire, USA). The conferences, limited to 100-120 participants, are organized in New England or its vicinity during the summer. They are scheduled in alternation with the IUPAC Symposium on Photochemistry every other year, and take place in one of the GRC locations. Many French photochemists have experienced their American flavour.

Other more specialized associations are mentioned if the case arises (Table E).

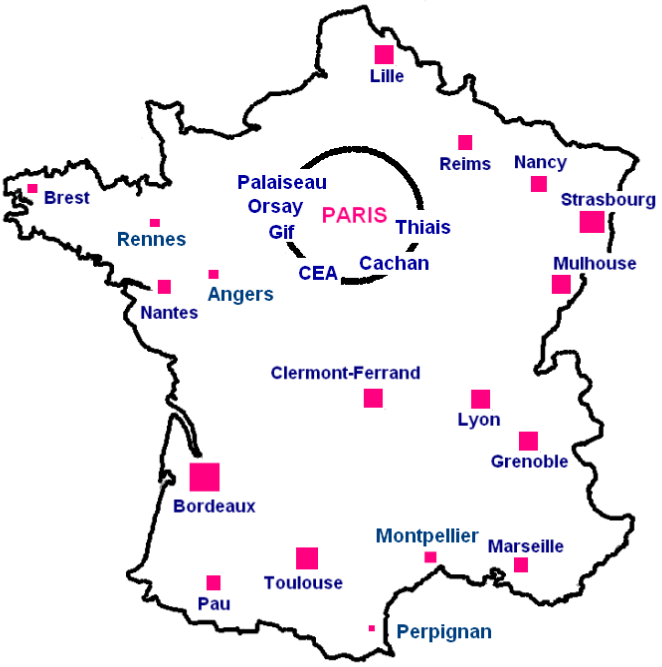

Figure 1. Main research centres in photochemistry and photophysics in France. Apart from the Ile-de-France, the square surfaces are arbitrarily proportional to the research activity between 1960 and *ca* 2015.

Photochemistry in "L'Actualité Chimique"

"L'Actualité Chimique" is the monthly magazine of the French Chemical Society which, since 1973, publishes annually ca 650 pages on all topics (fundamental or applied) related to chemistry. Some issues are devoted to special topics. An important issue on photochemistry was published in 1994 (Table B, a) on the initiative of the Club Electricité De France (EDF, Table A,c) managed by Christian Bailleux and Jean Faure. This was followed by three other special issues in 2007 and 2008 (Table B, c,d,e) showing the progress accomplished since 1994.

On the occasion of the International year of light (2015) Thomas Gustavsson and Jacqueline Belloni coordinated a special issue entitled “La Chimie fête la lumière” (Gustavsson and Belloni, 2015, Table B,f).

Tour de France

Accounts on photochemistry are generally organized by topics, as in the special issues of "L'Actualité Chimique" (Table A, a-e). The approach selected in the following pages is a visit of the reseach centres (Figure 1) to observe how the regions reflect their activities. The reader is invited to a "Tour de France" across the different "Régions" as delimited before 2016, namely: Ile-de-France, Bretagne-Pays de la Loire, Aquitaine, Midi-Pyrénées, Languedoc-Roussillon, Provence-Alpes-Côte d'Azur, Rhône-Alpes, Auvergne, Alsace, Lorraine, Champagne-Ardenne, Nord-Pas-de-Calais.

Ile-de-France

PARIS

ESPCI (Ecole Supérieure de Physique et Chimie de la ville de Paris)

The founders of the photochemistry laboratory at the ESPCI were *Emschwiller* and *Dufraisse* already mentioned above. *Jean Rigaudy* (who trained a number of students such as *Pierre Courtot*, *Georges Cauquis*, *Jean Santamaria...*) deepened and extended *Dufraisse*'s work, becoming the recognized specialist of acene photooxygenation and the photoreactivity of the resulting endoperoxides. In 1967, at the IUPAC Symposium of Enschede (The Netherlands) he was invited to give a plenary lecture entitled "Photooxidation of Aromatic Hydrocarbons" (Rigaudy, 1968). He also wrote the conclusion of "Photochimie 1994" in L'Actualité Chimique (Table B,a, pp 2008-2009); of note is the participation of *Guy Rio* (co-worker of Dufraisse at Collège de France) to this field: photooxidation of heterocycles, conjugated dienes and arylethylenes. Then, with *Santamaria*, *Rigaudy* developed electron transfer reactions in syntheses. Santamaria was invited to give a lecture at the 15th IUPAC Symposium, Prague entitled “Photoinduced electron transfer in organic synthesis. Application to alkaloids”(Santamaria, 1995). *Rigaudy* and *Kossanyi* were among the first to teach photochemistry at the master’s level at Paris University. *Janine Cossy*, coming from *Jean-Pierre Pete*'s school in Reims, succeeded *Rigaudy* in 1990, directing with talent her laboratory to the total synthesis of complex molecules (of therapeutic properties) using one or several photochemical key steps (Table B,a pp 25-33). *Catherine Vermeil* and her group (*Jeannine Masanet*, *Lucette Hellner*, *Janine Fournier*, *Christiane Lalo*) after a thesis under *Leach*'s supervision in Orsay (Hagege *et al.*, 1965) studied far UV photolysis of small molecules or free radicals (C_6H_6, SO_2, CH_4, NH_3, ND_3...) (Hellner *et al.*, 1971; Masanet *et al.*, 1973). *Clément Troyanowsky*, after investigating the photodimerisation of allenes, discovered with *Pierre Valat* in 1974 a so-called “new type of photochemical reaction”: the multiphotonic photodestruction through polychromatic irradiation, depending on flash intensity and duration (Gans *et al.*, 1976).

ENSCP (Ecole Nationale Supérieure de Chimie de Paris, Paris-Tech)

Daniel Lincot investigated the use of electrodeposition to build thin films of chalcogenides, metal oxides, tellurides... or polymetallic materials in order to fabricate solar cells. In 2011, he wrote an article entitled "photovoltaic energy: a responsibility for the chemists" in "L'Actualité Chimique" (Lincot, 2011); the expansion of the fundamental and applied research in this field is attested by the creation of the “Institut Photovoltaïque Ile-de-France (IPVF)” that will be accommodated in a new building on the Paris Saclay campus (Lincot, 2016). *Thierry Pauporté* and his team develop research in electrochemistry and interfacial chemistry oriented towards organic and inorganic photovoltaic systems. (Le Bahers *et al.*, 2011). *Michel Mortier* (Institut de Recherche de Chimie) leads a group dealing with the conception and characterization of transition metal ions or lanthanides doped materials for optical applications (Cordier *et al.*, 2015).

CNAM (Conservatoire des Arts et Métiers)

Bernard Valeur, after obtaining his thesis at the ESPCI in 1975 under the supervision of *Lucien Monnerie*, was appointed to the chair of general chemistry of the CNAM. His research in fluorescence, a burgeoning field, are recognized worldwide. He is the co-author of "Molecular Fluorescence. Principles and Applications", published in 2001 and reedited in 2012 (Table C,p). His expertise is also attested by his editorship in the "Journal of Fluorescence" (Table D,e) as well as his presence in the editorial board of the "Journal of Photochemistry and Photobiology" (Table D,b). *Valeur* is also known as author of bestsellers on colour and light (Table C,q,t,u). He was co-organizer in 1999 of an international conference on fluorescence in Paris (Table E,i). Among his accomplishments, he designed new supramolecular photoresponsive systems (Valeur *et al.*, 1992; Valeur and Leray, 2000) to carry out photoactive devices and fluorescent sensors for the selective detection of cations in biological media and in the environment (Table B,a pp 182-207; Table B,b pp 94-119). His demonstration of the reversible photoejection of lithium and calcium cations from a crown ether in the excited state is remarkable (Martin *et al.*, 1993). *René Lapouyade* (Bordeaux) independently obtained similar results with a related system (Table B,a pp 192-193). *Valeur*'s team was linked to the photochemistry laboratory of Cachan (*vide infra*) in 1995 where he continued his activities, particularly with *Isabelle Leray*. At the CNAM and Cachan, *Elisabeth Bardez* studied photoinduced proton transfer in amphoteric difunctional compounds (Bardez *et al.*, 1999) and is coauthor of the book "La lumière et la vie" with Valeur (Table C,u).

MNHN (Museum National d'Histoire Naturelle)

Pierre Douzou (Douzou *et al.*, 1961), a well known enzymologist, studied the solvent and temperature effect of the action of light on cytochrome P450 by flash photolysis (Bonfils *et al.*, 1979). *René Bensasson*, in Orsay, used flash photolysis as early as 1971 (Bensasson and Land, 1971; Amand and Bensasson, 1975). At MNHN, he took advantage of his expertise to make a major contribution (with *Michel Rougée*, *Christina Salet* and *Thérèse Montenay-Garestier*) to identify the primary species in photosynthesis, in nucleic acids photodegradation, and later of irradiated fullerenes, often in cooperation with other teams (Quaranta *et al.*, 2014). With *Rougée*, he uncovered the mechanisms of carotenoid photochemistry, particularly of their photooxidation. *René Santus* (also associated to the Amiens (CHU) "Centre Hospitalier Universitaire") investigated, in cooperation with

Michel Aubailly and *Marc Bazin*, the sensitized photooxidation of tryptophane and other amino acids (Walrant and Santus, 1974) as well as the *in vivo* interactions of photoactives porphyrins with fibroproteins as anticancer agents (Candide et al., 1986). His works on the photophysics of psoralens, with *Jean-Claude Ronfart-Haret* are also worthy of note. The latter joined *Kossanyi* at Thiais (*vide infra*). *Claude Hélène* and his group (*Thérèse Montenay-Garestier*, *Michel Rougée*, *Daniel Brault*, *Trung Le Doan…*) were an authority in the field of nucleic acids: specific sequences, photogenerated cross-links, breaking of DNA double helix under UV irradiation (Le Doan *et al.*, 1987). *Inter alia*, *Hélène* contributed to the use of intercalating molecules for the repair of DNA lesions.
In parallel, he was director (1974-1982) of the CNRS Molecular Biophysics Centre of Orléans.

Collège de France

After *Dufraisse* (*vide supra*), photochemistry returned to the Collège de France with *Pierre Joliot* (member of both the French and American Academies). *Joliot* largely contributed to discover the complex mechanisms of photosynthesis (Joliot *et al.*, 1969) many years before the three dimensional structure of a photosynthetic centre was established by Johann Deisenhofer, Robert Huber and Hartmut Michel (Nobel prize in chemistry, 1988).

ENS (Ecole Normale Supérieure, rue d'Ulm)

Yves Meyer played an important role in the development of transient spectroscopy in France, along with *Lars Linqvist* at Orsay (*vide infra*). He was one of the first to devise dye lasers (rhodamine 6G in aqueous solution (Crozet and Meyer, 1970)) and is known for his original work on subpicosecond systems (Martin *et al.*, 1985). *Monique Martin*, (Martin, 1974), endowed with a wide experience in the field of ultrafast spectroscopy (Orsay, Canada, Japan) has described solvation dynamics in the relaxation kinetics (Changenet *et al.*, 1997). She was the right person to chair, together with James T. Hynes, in 2003, the "6th International Conference on Femtochemistry", in Paris (Table E,j). Her recent work, with *Pascal Plaza* and *Pascale Changenet-Barret*, concerns the photoactive yellow protein (Changenet-Barret *et al.*, 2005). *Ludovic Jullien* (thesis with Jean-Marie Lehn, Collège de France), professor at the Université Pierre et Marie Curie, is well-known for his investigations in two photon photochemistry (Gagey, 2007) applied to medical imaging (Gauthier *et al.*, 2014). *Damien Baigl* (thesis 2003, Paris VI) develops photochemical reactions in microdrops to perform optical experiments (Venancio-Marques and Baigl, 2014; Anyfantakis and Baigl, 2014) or dynamic photocontrol (DNA structure).

UPMC (Université Pierre et Marie Curie or Paris 6)

Centre de Mécanique ondulatoire Appliquée (CMOA)

The theoretical chemistry of excited states was one of the domains of investigation of the CMOA, led by *Raymond Daudel*. The latter was, in 1967, a co-founder of the "International Academy of Quantum Molecular Science" (Daudel, 1967). In *Daudel*'s group, *Odilon Chalvet*, cooperated with several laboratories of experimental photochemistry, particularly for the calculation of pKas in the singlet and triplet excited states (Bertran *et al.*, 1969) and for establishing a theoretical approach of photooxygenation (Chalvet *et al.*, 1970). A member of this laboratory, *Earl M. Evleth*, made a major contribution to the photochemistry of some molecular Rydberg states, where an electron is removed to a distant orbital (ammoniac, amines, alcohols, water...) (Kassab *et al.*, 1983).

Laboratoire de Chimie Théorique

Alain Sevin, trained by *Alain Devaquet* (*vide infra*) to theoretical chemistry, contributed with *Bernard Bigot* and *Devaquet* towards the extension of the Woodward-Hoffmann rules in photochemistry (*vide infra Lionel Salem*), (Devaquet *et al.*, 1978). He later calculated numerous diabatic and adiabatic potential energy surfaces of singlet and triplet states of diverse molecules. With *Patrick Chaquin*, he expanded his research to the excited deactivation of lithium and magnesium by methanol (Chaquin *et al.*, 1990). Incidentally, *Sevin* is co-author of a book on the history of chemistry (Sevin and Dezarnaud Dandine, 2014).

Laboratoire de Chimie Organique Structurale (led by Jean-Jacques Basselier)

Jean Kossanyi (with *Bernard Furth*, *Jean-Pierre Morizur*, *Bernard Guiard*, *Patrick Chaquin, Jean-Pierre Le Roux*) studied in depth the mechanism of photochemistry of cyclanones and unsaturated aldehydes and applied these reactions as key steps in the syntheses of natural products such as grandisol, fragrantrol, exobrevicomine...(Chaquin *et al.*, 1977). Kossanyi was invited to give a plenary lecture at the IUPAC Symposium of Leuven in 1978, entitled "Photochemical Approach to the Synthesis of Natural Products" (Kossanyi, 1979). On proposal from the CNRS (Centre National de la Recherche Scientifique), Kossanyi moved to Thiais (*vide infra*) in 1980, to set up the "Laboratoire de Photochimie Solaire".
The observation of the stereospecific photoaddition of methanol to a double bond by *Jean d'Angelo* in 1980 in a nearby laboratory deserves to be emphasized (D'Angelo *et al.*, 1983).

Laboratoire "Acides Nucléiques et Biophotonique"

Daniel Brault (with *Christine Vever-Bizet* and *Stéphanie Bonneau*) has investigated the photosensitizing properties of chlorines in solution and in models of membranes (Mojzisova *et al.*, 2009).

Institut de Systématique, Evolution, Biodiversité (ISyEB)

Marie-Christine Maurel studies the stability of nucleic acids (RNA) under solar irradiation in a planetary environment, showing, *inter alia*, the role played by NaCl on the origin of planets and life (Vergne *et al.*, 2015).

Laboratoire "Réactivité de Surface"

Michel Che used the photoluminescence of numerous inorganic solid catalysts to characterize their activity (Chizallet *et al.*, 2008).

Institut Parisien de Chimie Moléculaire

In *Michel Verdaguer's* laboratory, *Valérie Marvaud* has applied the photomagnetism to molecules of the MoCuX family (Ciofini *et al.*, 2007). These works were developed in parallel to those of Bordeaux and Toulouse (*vide infra*).

The work of *André-Jean Attias* (Chimie des Polymères) also covers supramolecular luminescent systems (some of them emit blue light) for materials displaying optoelectronic properties. (*vide Baldeck*, Grenoble, *Andraud*, Lyon, *Nicoud*, Strasbourg).

Université Denis Diderot

Interfaces, Traitements, Organisation et Dynamique des Systèmes (ITODYS)

François Maurel (director of ITODYS) and his team are using *ab initio* computational methods, often in cooperation with *Denis Jacquemin* (*vide* Nantes), to study diverse chromophores and photochromic systems, especially diarylethylenes (Perrier *et al*., 2012).

Other Universities

At Paris XII, *Marie-Claire Gazeau, François Raulin* and their co-workers are dealing with planetary space photochemistry, in search of prebiotic and biological molecules (Table B c, XIX-XXIV).
At Cergy-Pontoise, *Jean-Louis Lemaire* and his group (Laboratoire d'Etudes du Rayonnement et de la Matière en Astrophysique et Atmosphères, LERMA), investigate the mechanism of molecules (such as H_2) formation, on the interstellar dust grains (Table B,c III-IX).

Orsay (Université Paris XI)

Moving from the "Laboratoire de Chimie Physique" in Paris in the 1960s, *Michel Magat* and *Sydney Leach* divided up their activities into two laboratories, described as follows.

Laboratoire de Physicochimie des Rayonnements (led by Michel Magat)

A half of this laboratory's research concerned photophysics and photochemistry. After *Magat*'s death (Bensasson, 1978; Joussot-Dubien, 1978), *Jean Faure* was appointed director in 1979 and moved to Cachan in 1989.

Rose Marx with her team (*Tom Govers, Gérard Mauclaire, Renée Derai, Joël Lemaire*, *Michel Heninger, Serge Fenistein*) were devoted mainly to the formation of excited species in the gaseous state and the study of their internal energy (electronic, vibrational and rotational). This often resulted from ion-molecule reactions and, to that end, they used, *inter alia*, the LURE synchrotron radiations (Fenistein *et al.*, 1990). This research has a strong interest in astrophysics.

Under *Magat*'s impetus, *Pierre Cordier* and *Jacques Delaire* set up a nanosecond pulsed radiolysis instrument and studied, with *Jacqueline Belloni*, solvated electrons in liquid ammonia and amines. *Belloni* and her team (*Mehran Mostafani, Jean Amblard, Jean-Louis Marignier*) developed radiation chemistry, that is often the companion of photochemistry and allows to deepen many chemical and biochemical mechanisms, as explained in "L'Actualité Chimique" (Table Bd, II-XX)). Applied to photography, radiation chemistry allowed *Belloni* and her co-workers to discover the mechanism of development of the latent image in its silver salt emulsion, as reported in the literature (Mostafavi *et al.*, 1989; Belloni *et al.*, 1991) and described by *Marignier* in "L'Actualité Chimique" 2007 (Table B,a pp 85-89). *Mehran Mostafavi* is co-author with *Thomas Gustavsson* (*vide infra*) of a book on ultra fast reactions published in 2007 (Table C,r).

Jean Faure has tackled different aspects of photophysics and photochemistry with *Ivan Kraljic, Nina Ivanoff, Lydie Grajcar, Fernand Kieffer* and *Jacques Delaire. Kraljic* used some dyes as sensitizers of solar cells. He also got a better understanding of the cyanines properties in dye lasers and singlet oxygen sensitizers (with *Graljar, Ivanoff* and *Faure*).

Delaire (with *Fernand Kieffer, Claudette Lapersonne-Meyer* and *Jean Faure*) studied the photoionization and the electron transfer in rigid matrices (glasses, polymers) with special emphasis on electrons and holes trapping. Biphotonic photochemistry was also developed (1979-1989).

Tom Govers and *Odile Dutuit* were interested in the unimolecular decay of small ionized molecules, using the LURE synchrotron, whereas *Jacques Bullot*, *Monique Gauthier*, *Pierre Cordier* and *Odile Gallais* studied the photoluminescence of amorphous semi-conductors. *Jacques Roncin* (with *Lydia Bonazzola, Nicole Leray, Jean-Pierre Michaut*) determined the structure and reactivity of radicals produced by photolysis of single crystals and molecular solids.

Laboratoire de Chimie Théorique

Magat invited *Lionel Salem* (PhD thesis in 1960, supervised by Hugh Longuet-Higgins, Cambridge, England) to build a group of theoretical chemistry, partly oriented towards the study of electronically excited states. Whereas the Woodward-Hoffmann rules took only the ground state into account, *Salem* published the first correlation diagrams for the excited states (Salem *et al.*, 1973; Salem, 1974; Dauben *et al.*, 1975). *Salem* coined the concept of "sudden polarization" for a neutral alkene, becoming abruptly dipolar after torsion of the double bond in the first excited singlet state (expected to occur in the vision). This result led him to cooperate with *Joussot-Dubien* (Bordeaux, *vide infra*). Salem was named a member of the "International Academy of Quantum Molecular Science" (Daudel, 1967) and launched, with the CNRS, the "Nouveau Journal de Chimie" (Salem, 1977). He trained a number of theoreticians, among them *Alain Devaquet* (thesis in 1972, minister of universities in 1986) who was himself supervisor for the thesis (1979) of *Bernard Bigot* (Devaquet *et al.*, 1978); *Bigot* became an administrator of the highest ranking: head of the Ecole Normale Supérieure Lyon, the CEA (Commissariat à l'Energie Atomique) and ITER (International Thermonuclear Experimental Reactor). Then *Devaquet* trained *Alain Sevin* to theoretical photochemistry; the latter took over Devaquet in the field, while cooperating with the *Daudel* group (UPMC, *vide supra*).

Equipe de Recherche "Processus Photophysiques et Photochimiques"

This team was formed after the closure of professor Cauchois' laboratory at Orsay. It belongs to the "Laboratoire de Physicochimie des Rayonnements" and was composed of *Annette Bernas, Edmond Amouyal, Dora Grand and Simone Hautecloque*. *Bernas* (with *Grand* and *Hautecloque*) focused her studies on photoionization of the solid state in organized media. (Bernas *et al.*, 1972; Hautecloque *et al.*, 1985). *Simone Hautecloque* contributed to the study of atmospheric pollution, in describing the photochemical decomposition of ozone and freons as well as the formation of HOCl. She also investigated low

temperature (4-20 K) solid state photolysis, obtaining xylyl biradicals as identified through their high resolution fluorescence spectra.
Edmond Amouyal, (thesis 1976, Orsay) cited above for his commitment in the French Group of Photochemistry (Table A,a) started his research career with *Bensasson* at Orsay and became later one of the pioneers of the water photolysis (with *Henri Kagan* and *Alex Moradpour*), using in particular electron transfers in Ru (II) complexes (Moradpour *et al.*, 1978) in parallel with research works of *Jean-Marie Lehn* and *Jean-Pierre Sauvage* at Strasbourg (*vide infra*). *Amouyal*'s activities were then directed towards supramolecular photochemistry (Table B,a pp 194-207) and solar energy (Amouyal, 1995). He also coordinated three major articles on solar energy of the future in "L'Actualité Chimique" in 2007 (Table B,b pp 40-60). He is now in the "Laboratoire des Solides Irradiés" at the Ecole Polytechnique (*vide* Palaiseau).

Laboratoire de PhotoPhysique Moléculaire (LPPM) (led by *Sydney Leach*)

Sydney Leach founded the laboratory in 1967; it was composed of four teams led by *Leach*, *Lefebvre*, *Legay* and *Lindqvist* who took different paths. In 2001 the LPPM was directed by Philippe Bréchignac and is now a part of the ISMO (Institut des Sciences Moléculaires d'Orsay) since 2010. In 2013, Bernard Bourguignon succeeded Bréchignac at the head of ISMO.
Leach set out to experimentally study electronic structures, molecular dynamics and reactivity of ions, radical-ions and molecules in gaseous and solid phases. In the following are mentioned the accomplishments of some members of his group (*Gérald Dujardin, Guy Taieb, André Tramer, Joëlle Rostas, Marcel Horani, Claudina and Daniel Cossart, Eva Migirdicyan, Benoît Soep, Françoise Lahmani, Christophe Jouvet, Alain Desprès, Violen Lejeune, Dolorès Gauyacq, Séverine Boyé-Péronne*...).
Gérald Dujardin and *Guy Taieb* used coincidence techniques to investigate intramolecular interactions of polyatomic ions with the LURE synchrotron. *Dujardin* has studied non radiative transitions with *Leach* (Dujardin and Leach, 1983). Such research was also conducted by *André Tramer*, especially on intersystem transfer in isolated molecules, in emphasizing theoretical developments.
Joëlle Rostas and *Marcel Horani* have applied high resolution spectroscopy to the study of interaction between vibrationic states.

Claudina Cossart and *Daniel Cossart* showed particular interest to molecular ions such as CO_2^+, N_2O^+, COS^+ and to polyfluoro benzenes in gaseous phase.

Eva Migirdicyan (with *Sydney Leach, Alain Desprès, Violen Lejeune*) became well-known in the 1950s for isolating the first photoisomers of benzene and several of its derivatives in solid matrices (Leach *et al.*, 1959). She has notably studied the spin-orbit interactions of carbonyl aromatic compounds in mixed crystals at very low temperatures.

In connection with photophysical and photochemical problems regarding autoionization processes (*Christophe Jungen*), their competition with predissociation (*Anick Giusti*), energy redistribution in the photodissociation in molecules (*Roland Lefebvre*) and van der Waals complexes (*Alberto Beswick*), several theoretical studies for the coupling between discrete states and continuum and quasi continuum were achieved.

Benoît Soep (*vide* CEA) has applied ultrafast laser spectroscopy to the study of weakly bound van der Waals complexes (*v.g.* glyoxal-rare gases) considered as analogs of collisional relaxations.

Françoise Lahmani (thesis in 1970 with *Nina Ivanoff* in the Magat laboratory on diazirines photoisomerizaiton) joined *Leach*'s team in 1973. She studied the photodissociation of nitroso derivatives (organic nitrites, nitrosyl halogenides) in the V-UV region (Synchrotron) followed by the fluorescence of excited NO fragments. More recently, *Lahmani* explored molecular fluorescence in supersonic jets, especially with *Anne Zehnacker* (whose thesis she supervised in 1988). The latter continues these works, notably on chiral van der Waals complexes (Le Barbu *et al.*, 2002). This original research was described in "L'Actualité Chimique" in 2004 (Seurre *et al.*, 2004). In 1985, *Lahmani* was editor of "Photophysics and Photochemistry above 6 eV" (Table C,c) and, in 2005, co-editor, with *Tramer* and *Jungen* of "Energy Dissipation in Molecular Systems" (Table C,s). This editorship is in keeping with her expertise in non exponential fluorescence kinetics (Lahmani *et al.*, 1974).

Christophe Jouvet has applied femtosecond lasers to examine the non radiative deactivation of π-σ^* excited states in aromatic biomolecules, showing the role of tryptophane in the photobridging between protein and DNA (Table B,b pp 15-18). *Antonio Lopez-Campillo* studied (1978-1980) the kinetics of excited deactivation of indoles and derivatives in low temperature glasses.

Leach, in addition to the above-cited works, developed research in interstellar photochemistry owing to his expertise in vacuum UV spectroscopy. An account on this topic, coordinated by *Leach* and *Amouyal*, was published in "L'Actualité Chimique" in 2008 (Table B,c). *Leach* contributed to the spectroscopic studies of fullerenes (Quaranta *et al.*, 2014). *Dolorès Gauyacq* (with *Séverine Boyé-Péronne*) carries out research on the photolysis of small hydrocarbons in circumstellar or comet atmosphere (Table B,c X-XV). In addition, the research developed in the Institut d'Astrophysique Spatiale by *Louis Le Sergeant d'Hendecourt* on prebiotic photochemistry in interstellar media can also be noted (Le Sergeant d'Hendecourt and Meinert, 2015).

Lars Lindqvist (with *Arlette Kellmann, Marie-Christine Duval, Marie-Pierre Fontaine-Aupart, Francis Tfibel, Monique Martin*) has been a *pioneer* of flash photolysis, initially on the microsecond scale, in 1967 (Kellmann and Lindqvist, 1967) and then in the nanosecond domain in 1971 (Lindqvist and Lutz, 1971). Lindqvist was one of the precursors of the study of primary processes of excited molecules in solution (exciplexes, photochromism) and of the two photon excitation (with *Bonneau* and *Joussot-Dubien* in 1968, *vide infra*). Later, he developed investigations (notably with *Tfibel*) in photobiology (Lindqvist *et al.*, 2010).

Marie-Claire Fontaine-Aupart (with her team, especially *Francis Tfibel* and *Sandrine Lévêque-Fort*) has applied "photonics" (generation, transmission, detection of photons) to observe closely biological media. It consists of using a two photon microscope to analyse the fluorescence lifetimes in real time; this method allows, for example, the early diagnostic of a bladder cancer. An article appeared in « L'Actualité Chimique » in 2003 (Lévêque-Fort *et al.*, 2003).

René Bensasson (initially researcher in the antenna of Yvette Cauchois's laboratory at Orsay) is an expert in laser flash photolysis. He left Orsay to join the Museum National d'Histoire Naturelle (MNHN) in Paris (*vide supra*).

Laboratoire Aimé Cotton

Jean-Pierre Galaup, after cooperation with *Hans Peter Trommsdorf* (*vide* Grenoble) has studied spectroscopy in solid matrices (hole burning, holography, photolithography). He has more recently used "optical tweezers" to handle nanoobjects under microscope (Rodriguez-Otazo *et al.*, 2009).

Institut Curie

Laboratoire de Biophysique et Radiobiologie (led by Jean-Marc Lhoste in 1981)

Daniel Lavalette (with *Catherine Tétreau* and *Michel Momenteau*), following spectroscopic studies of excited states of aromatic compounds, oriented his research towards hemochrome photochemistry (Lavalette *et al.*, 1979).
Dietrich Averbeck has been an expert in biophotochemistry of furocoumarines and cancer photochemiotherapy (Averbeck *et al.*, 1978). He wrote several authoritative reviews (1989-2008) on the biological effects of chemical substances.
Bernard Muel became well-known for his pioneering works on triplet-triplet annihilation and other research on cancerogenic hydrocarbons and their presence in the atmosphere; he also examined the influence of the UV irradiation wavelength of DNA on cancer formation (Kulucsis *et al.*, 1999).
Pierre Valat and *Hervé Tourbez*, using a 30 picosecond pulsed laser, analysed, *inter alia*, the tryptophane fluorescence in hemoglobin.

Unité "Stress Génotoxique et Cancer"
Equipe de biologie des radiations

This team, one of the 6 teams of the unit, led by *Evelyne Sage,* was formed in 1995 in Paris and installed in the Orsay site of the Institut Curie, in 1999. *Sage* (thesis in 1981 in biophysics at Orléans) is well known for her research (presently with *Pierre-Marie Girard*, on the biological damages due to UV radiations, such as DNA lesions and their mutagenic consequences (Sage, 1993). She is member of the editorial board for "Photochemical and Photobiological Sciences" (Table D,d) and was vice-president (2009-2011) then president (2011-2013) of the "European Society for Photobiology (ESP)" (Table A,f). Sage is president (since 2008) of the French Society of Photobiology (SFPb) (Table A,e). She organized several international conferences in Europe and the USA, particularly the "11th Congress of the ESP" at Aix-les-Bains (France) in 2005 (Table E,m).

ICMMO (Institut de Chimie des Molécules et Matériaux d'Orsay)

Pei Yu (with *Anne Léaustic*) employs the photochromic properties of materials for the reversible storage of information, in cooperation with *Keitaro Nakatani* (*vide* Cachan). *Anne Bleuzen* (with *Amélie Bordage* and *Giulia Fornasieri*) carries out and studies multifunctional, commutable hybrid materials for high density optical memories.

Gif-sur-Yvette (Laboratoire des Substances Naturelles du CNRS)

Although in this large centre research is focused mainly on ground state chemistry, photochemistry was represented by *Charles Giannotti* and *René Beugelmans*. The first was active in the photochemical reactivity of organometallic compounds; he realized dioxygen (Mérienne *et al.*, 1973) or sulphur insertion into cobalt-carbon bonds through irradiation of alkoxycobalt-oximes and tungsten insertion into a C-H bond by photolysis of tungsten complexes. *Giannotti* has also particularly studied closely the cytotoxic activity of tetrapyrrolic complexes of transition metals (polyoxoanions, such as sodium decatungstates). *Beugelmans* was notably interested in heterocyclic photochemistry, devising an elegant synthesis of a number of heterocycles by photoinduced radical chain nucleophilic substitution (SRN_1) (Beugelmans and Roussy, 1979; Beugelmans *et al.*, 1979).

Thiais

Laboratoire de photochimie solaire

This laboratory, born in 1980, constituted a unit of the Thiais CNRS Centre. It was led by *Jean Kossanyi* and *Francis Garnier*. The latter became famous (with *Denis Fichou*) for his work on the first organic field effect transistors (Garnier *et al.*, 1990) and on photovoltaic cells, especially organic-inorganic hybrids (Fichou, 2000; Videlot *et al.*, 1999). *Jean Roncali* has pursued this research at Angers (*vide* Angers). *Kossanyi* (*vide supra*) known as president of the French Group of Photochemistry (Table A,a), editor of EPA NL and co-organizer of the first EPA summer school (Table A,b), also chaired several international conferences (Table E,a,e,f; Schaffner, 2002; Wilkinson, 2003). He started research at Paris VI (UPMC) in examining structure-photoreactivity of ketones and enones (*vide* Paris). At Thiais, he designed and synthesized charge transfer systems that he studied using ultra fast spectroscopy with *Joseph Pouliquen, Pierre Valat and Véronique Wintgens* (Wintgens *et al.*, 1994). Later, his team took an active interest in the photoconductivity and photoluminescence of semi-conducting ceramics, doped with transition metals (Kossanyi, 2003).

Cachan (Ecole Normale Supérieure)

Laboratoire de Photophysique et de Photochimie Supramoléculaire et Macromoléculaire
(PPSM)

In 1989, the Cachan Ecole Normale supérieure recruted *Jean Faure* to create a research group in photochemistry. *Faure* (thesis in Bordeaux, supervised by *Joussot-Dubien*) had founded an important laboratory at Mulhouse and succeeded *Magat* at Orsay (*vide* Orsay, Bordeaux and Mulhouse). He was joined by *Jacques Delaire* (thesis at Orsay, supervised by *Magat* and *Marx*), *Robert Pansu* (thesis at Orsay, supervised by *Faure*) and *Keitaro Nakatani* (thesis at Orsay, supervised by Olivier Kahn), in 1993. *Faure* made himself known, since the beginning of his research, as an advocate for the use of lasers to investigate the mechanisms of photochemical reactions of monomers and polymers (Faure, 1977). His laboratory became associated to CNRS in 1995 and took the name of PPSM. It developed rapidly to include up to 40 persons.

Faure and *Delaire* have developed research in diverse area related to molecular materials such as "photoresists", polymer matrices of photochromic compounds for non-linear optics, (Delaire and Nakatani, 2000), fluorescent organic materials, biphotonic photoionisation in artificial vesicles, and also, nanoparticles and nanocomposites. *Delaire* was coordinator of the article "Photochemistry of Molecular Materials from Yesterday and to-Day" in “L'Actualité Chimique" in 1994 (Table B,a pp 83-131) and, with *Jean-Pierre Desvergne* (*vide* Bordeaux) of the chapter on "Molecular Materials and Photonics" in 2008 (Table B,e pp 31-50). *Pansu* carried out irradiation under microscope (3D) with a titane-sapphire laser, femtosecond laser ablation and a device for intracellular calcium determination. In 1994, *Valeur* (*vide* CNAM) joined the group with *Isabelle Leray*, recruted as "chargée de recherché au CNRS" in 1993, to develop supramolecular photochemistry (Souchon *et al.*, 2006). In 1998, *Delaire* succeeded *Faure* as head of the PPMS. The same year, *Pierre Audebert*, professor at Besançon University, was appointed at the laboratory, with his team specialized in electrochemistry and synthesis of electro- and photo-active molecules. In cooperation with the company "Crime Scene Technology", they designed the reactant "lumicyano" to detect finger prints (Prete *et al.*, 2013). *Gilles Clavier* (thesis Bordeaux, 1999) joined the group in 2001 as "chargé de recherche au CNRS" to strengthen the PPMS' ability in organic synthesis; his recent activities are focused on the realization of fluorescent organic nanoparticles exhibiting a strong brightness (Grazon *et al.*, 2013). With *Rachel Meallet-Renault* , appointed "maître de conférences" in 1997, and *Rémi Métivier*, appointed "chargé de recherches" in 2005, *Pansu and Nakatani* have developed photochromic nanoparticles capable of giant commutation for image super-resolution (Métivier *et al.*, 2009).

Nakatani has managed the French GDR ("Groupe de Recherche Photochromisme"), becoming international in 2006 (with Germany, Russia, Japan and China). It is composed of about 150 researchers whose 17 teams in France (notably: *Nakatani* and *Métivier* (Cachan), *Maurel* (Paris), *Yu* (Orsay), *Debaere and Sliwa* (Lille), *Ishow* (Nantes), *Pozzo* and *McClenaghan* (Bordeaux), *Micheau* and *Coudret* (Toulouse), *Lokshin* (Marseille). Under the Group auspices, *Micheau* organized an international colloquium (80 participants) in Corsica, 23-27 November 2015, entitled "Photoswitched Molecular Systems and Devices, from synthesis to applications". *Robert Guglielmetti*, a pioneer of photochromism in France (*vide* Marseille) met with great public acclaim.

Saclay

CEA (Commissariat à l'Energie Atomique)
Renamed "*Commissariat à l'énergie atomique et aux énergies alternatives*" since 2009.
The laboratories below belong to "Direction Scientifique de la Matière" (DSM)

Their organization and names have changed with time.

Département de Physico-Chimie

A great part (*ca* 30 persons in 1981) of this laboratory, led by *Paul Rigny*, was devoted to photophysics and photochemistry. The interaction photon-matter concerned continuous or picosecond pulsed irradiation, from vacuum UV to far infrared wavelengths; in addition to classical sources, synchrotron radiation was also used. Investigations were conducted in (1) condensed phase and (2) in gas phase.

1- condensed phase

Paul Rigny (thesis in physics at Orsay in 1967) is a specialist of the chemistry and photochemistry of uranium, especially the fluorides (UF_6, UF_4) of which he studied the dissociation under UV irradiation (Alexandre *et al.*, 1983). *Rigny* is also well-known for his editorials and other articles in "L'Actualité Chimique" where he was editor in chief, and as co-author of books on the impact of chemistry upon society (2005-2014, EDP publishers). *Gérard Folcher* studied (mainly with *Rigny*) the photochemistry of salts (such as XeF_4, $XeOF_4$, UF_6) and organic complexes of uranium as well as porphyrins (with *Jean-Claude Mialocq, Jean-Pierre Le Roux, Michel Cauchatier*, *Christian Angelié*, *Oleg Anitoff*). *Jack Sutton* (with *Bernard Hickel and Thu Hoa Tran Thi*) worked on describing the mechanisms of electron transfer using picosecond flash photolysis, *inter alia*, in aqueous solutions of phenol or phenates. *Alain Barraud* (with *Michel Vandevyver*) examined the mechanism of spiranes isomerization in Langmuir-Blodgett layers, as well as the formation of photoresists. *Jean-Claude Mialocq* applied ultrafast kinetics techniques to the study of many mechanisms: fluorescence and isomerisation of dyes, photoionisation of ferrocyanides or phenolates, electron transfer and solvated electrons formation, as well as a number of molecules of biological interest, v.g. reactive centres in bacteria and carotenoporphyrins (Moore *et al.*, 1984). With *Thomas Gustavsson* and *Stanislas Pommeret*, *Mialocq*, using subpicosecond fluorescence, brought to light the first steps of dye excited states relaxation and solvent effects (Gustavsson *et al.*, 1998).

2- Gas phase

The research in this area concerns essentially multiphotonic ionisation, unimolecular dissociation of polyatomic ions and highly excited electronic states.

Early on, *Michel Clerc* was interested in vacuum UV photolysis of small molecules (Clerc and Barat, 1967). *René Botter* and his team (*Xavier Ripoche, Jacques Le Calvé, Iliana Dimicoli*) studied multiphotonic dissociation of SF_6, CF_3I... (Ripoche *et al.*, 1988). *Gérard Salvetat* (with *Iliana Dimicoli, Jean Jaraudias, Roland Bougon*) examined bimolecular reactions assisted by IR laser and two-photon ionisation. *Irène Nenner* with her team (*Paul Morin* and external co-workers such as *Philippe Millié*) explored a variety of species (di- and tri-atomic small molecules up to C_6F_6 and triazines) that, irradiated in vacuum UV, undergo photoionisation to mono- and even di-cations as well as photodissociation (Morin and Nenner, 1986). *Jacques Le Calvé* (with *Michel Mons, Iliana Dimicoli, François Piuzzi*) utilized the supersonic jet technique to examine van der Waals complexes (benzene-argon, rare gases-halogens) by biphotonic excitation (Mons *et al.*, 1990).

Laboratoire Francis Perrin (founded in 2001, recently incorporated the Laboratoire des interactions, dynamique et laser (Lidyl)

The Group "biomolécules excitées") named, in 2015, "Dico" (Dynamique et Interactions en Phase Condensée), led by *Dimitra Markovitsi*, belongs to the Laboratoire Francis Perrin.

Dimitra Markovitsi (engineering degree at Athens, 1978, thesis from Strasbourg in 1983) made herself known for her studies of the effect of organized media on photophysical and photochemical properties in liquid crystals and thin layers (Markovitsi *et al.*, 1991). Since 2001, she has focused her activities, first with *Thomas Gustavsson* (*vide infra*), then with *Akos Banyasz*, and *Pascale Changenet-Barret* to the photophysics and photochemistry of heterocyclic bases of DNA monomer and DNA helices (multichromophoric systems) (Markovitsi *et al.*, 2006). To that end, her team uses ultra fast (nano to femtosecond) kinetic techniques (Vaya *et al.*, 2010) in absorpsion and fluorescence as well as theoretical calculation in cooperation with *Philippe Millié* (Orsay, CEA), *Richard Lavery* (biochimie théorique, UPMC, Paris) and *Roberto Improta* (Naples University) (Bouvier *et al.*, 2003). This global approach has allowed a deep understanding of the damages to DNA caused by UV irradiation (Gustavsson *et al.*, 2006). In parallel, interactions of drugs with biomolecules have been scrutinized (Markowitsi, 2013). Recent results concern skin protection with melanins. Markowitsi was invited to give a plenary lecture in 2008 at Göteborg for the "IUPAC XXIIth Symposium on Photochemistry", entitled "Interaction of UV radiation with DNA helices" (Markowitsi, 2009). She was a member of the EPA executive committee (2004-2010), being elected president in 2007 (Table A,b). In 2007, she coordinated the theme "Les photodommages à l'ADN" in "L'Actualité Chimique" (Markovitsi, 2007).

Thomas Gustavsson (thesis in Stockholm, 1988, in high resolution spectroscopy) joined the laboratory after his thesis. In addition to important work with *Markovitsi*, he built pico and femtosecond lasers set-up to measure very low fluorescence intensities of DNA in the UV region. He co-authored an article in "L'Actualité Chimique", entitled "Femtochimie: de la molécule isolée à la phase liquide" (Gustavsson *et al.*, 2001) and a book in 2007 (Table C,r) on ultra fast reactions. *Pascale Changenet-Barret* joined the group recently.

Benoît Soep (first at Orsay, *vide supra*) was a pioneer in the study of ultra fast reactions, occurring in the femtosecond range, that allows to follow reactions in real time; he described time dependent wave packets, instead of stationary state reaction coordinates. He coordinated with *Yann-Antoine Gauduel* in 2008 an original article on femtochemistry in motion (Table B,e, pp 51-54), see also (Gauduel, 2001). With his team (*Lionel Poisson, Niloufar Shafizadeh*), he investigated the femtosecond electronic dynamics of complex molecules (Poisson *et al.*, 2006).

Thu-Hoa Tran-Thi investigated first energy and electron transfer in donor-acceptor complexes of porphyrins and phthalocyanines (Fournier *et al.*, 1999) and then devoted her research activities to "green chemistry" in solid matrices (zeolites, xerogels). She designed chemical nanosensors to detect selectively and evaluate traces of pollutants (BF_3, HCHO, NCl_3...) (Tran-Thi *et al.*, 2011). Her team developped devices now marketed under the name"Ethera".

Edifices Nanométriques (constitutes one of the research units of NIMBE: Nanosciences et Innovation pour les Matériaux, la Biomédecine, l'Energie)

Cécile Raynaud (head) and her group have obtained remarkable nanoparticles of photoluminescent silicon (Guillois *et al.*, 2004) using laser pyrolysis as described by *Nathalie Herlin-Boime* in "L'Actualité Chimique" in 2008 (Table B,e, pp 14-15). *Paul Mathis* is known as a specialist of the structural and functional aspects of photosynthetic reactive centres (Takahashi *et al.*, 1987).

Palaiseau (Ecole Polytechnique)

The school is famous for excellence in sciences, especially in mathematics. The creation of a laboratory in optics and biosciences is relatively recent. Several groups use spectroscopy and ultra fast techniques. *Jean-Louis Martin* and his team examine the functional dynamics of proteins at the femtosecond-picosecond timescales (Casanova *et al.*, 2007). *Marten Vos* (Vos, 2008) and *Andras Lukacs* study the DNA flavoprotein, a photolyase acting in the repair of major lesions caused by UV irradiation of DNA (Lukacs *et al.*, 2006). *Jean-Pierre Boilot* exploits rare earths or transition metals luminescence in nanoparticles as sensors in biology (Giaume *et al.*, 2008). In 2000, *Edmond Amouyal*, moving from Orsay (*vide supra*), started a team on "irradiated solids" to design and carry out functionalized photoluminescent nanoparticles.

Bretagne et Pays de la Loire

Brest (Université de Bretagne Occidentale)

After his thesis with *Jean Rigaudy* at the ESPCI *(vide supra), Pierre Courtot* founded a research group on photochemistry in the 1960s, and, a few years later, launched the " Groupe Français de Photochimie (GFP)", acting as an efficient president until 1985 (*vide supra* and Table A,a). His research area was that of conjugated dienes and trienes where, at that time, a major question arose about the orbital symmetry control in the excited state related to the ground state conformations (*vide Salem*, at Orsay). For his original contribution (particularly with *René Rumin* and *Jean-Yves Salaün*), he was invited to give a plenary lecture entitled "Photochemistry of polyenes. Control by orbital symmetry and ground state conformations?" in 1976 at the "VIth IUPAC Symposium", in Aix-en-Provence (Courtot *et al.*, 1977). In 1978, he was editor of a book “Eléments de Photochimie Avancée” (Table C,b).
Robert Guglielmetti, appointed "maître de conférences" in organic chemistry in 1971, synthesized a number of photochromic substances and studied their spectroscopic and photochemical properties. In

1983, he was appointed Professor at the University of Marseilles (*vide infra*).
More recently, *Christiane Carré*, coming from the Mulhouse laboratory of photochemistry (*vide infra*) where she had studied the microstructuration of photopolymerizable systems (mechanisms, procedures optimization) has carried out durable optical structures (patterns) at Lannion (Ecole Nationale Supérieure des Sciences Appliquées et de Technologie, ENSSAT), and at Telecom Bretagne.

Rennes (Université)

Mireille Blanchard-Desce (thesis with J.-M. Lehn at the Collège de France in 1989) created a research group on non linear optics (NLO). She designed and synthesized numerous organic molecules substituted with electron donor and acceptor groups and then nanosystems expected to show a cooperative effect (with *Olivier Mongin*, *Martinus H.V. Wertz*, *Francesca Terenziani...*) and biphotonic processes (Mongin *et al.*, 2002; Katan *et al.*, 2005). In 2011, she moved to the "Institut des Sciences Moléculaires (ISM)" in Bordeaux (*vide infra*). *Mongin* now pursues research along the same line in Rennes. *Cyril Poriel* devised new phosphorescent organic diodes (PhOLEDs) emitting in blue and green (Romain *et al.*, 2015) in cooperation with colleagues of Cachan, Gif-sur-Yvette and Palaiseau (*Bernard Geoffroy*). *Yann Molard* (thesis James Tucker, Exeter) leads a group of supramolecular photochemistry to synthesize transition metals nanocomposites and luminescent organic-inorganic hybrid systems in view of biomedical imaging. He recently showed that octaedric clusters of molybdenum in polyurethane, emitting in red and near IR, are good sensors for molecular dioxygen (Amela-Cortes *et al.*, 2015).

Nantes (Université)
Faculté des sciences et techniques de Nantes

Chimie et interdisciplinarité, Synthèse, Analyse, Modélisation (CEISAM)

Fabrice Odobel (with *Jérôme Fortage...*) is as an authority in the domain of organic photovoltaics (OPV). Of note, for instance, is the design and synthesis of strongly coupled electronic systems for long-distance charge separation (29 to 46 Å) (Fortage *et al.*, 2008). A solar cell, using nickel oxide sensitized with dyes (obtained in cooperation with Swedish researchers) was remarked (Gibson *et al.*, 2009). *Denis Jacquemin*, coming from Namur, Belgium, was appointed professor in Nantes in 2010 as a theoretical chemist specialized in the study of excited states. He and his team (*Agilaos Chantzis*...) cooperate with *Véronique Guerchais* and *Henri Doucet* (University of Rennes) (Kedong *et al.*, 2014). *Jacquemin* designed photochromic dyades for nanometric scale information storage (Fihey and Jacquemin, 2015). In 2014, he co-authored an interesting article on theoretical photochemistry with *Chantal Daniel* (*vide* Strasbourg) in "L'Actualité Chimique" (Jacquemin and Daniel, 2014). *Eléna Ishow*, after a thesis with Jean-Pierre Launay at Toulouse and two years teaching at Cachan, was appointed professor at the University of Nantes in 2010. With her team and together with several colleagues (such as *Véronique Guerchais, François Lagugné-Labarthet, Adrien Faucon, Steven Nedellec*...) she is involved in photosensitive nanomaterials, gold-coated photochromic organic nanoparticles, stable agents for imaging (Snell *et al.*, 2015; Faucon and Ishow, 2014). She also participates in cooperative programs with searchers fromParis.

Institut des Matériaux

Luc Brohan, with his team, improves TiO_2 based photosensitive solutions and gels for energy and storage conversion (Cottineau *et al.*, 2008).

Département de Physique

John Kessler and his co-workers carry out solar cells composed of mixed semi conductors, using the atomic deposition technique (Torndahl *et al.*, 2007).

Angers (Université)

Institut des Sciences et Technologies Moléculaires

Jean Roncali obtained a thesis under the supervision of *Garnier*, in 1984, on solar cells at Thiais (*vide supra*). Appointed at Angers in

1992, he pursued his research on the major topic of the Thiais laboratory: conducting organic polymers. He designed a variety of linear conjugated systems directed towards a wide range of applications such as energy storage, non linear optics, electroluminescent organic diodes (OLEDs), organic transistors and solar cells (Roncali *et al.*, 2014). His fame is attested *inter alia* by the success of his reviews (Roncali, 1992; Roncali, 1997) and his papers (*v.g.* Roquet *et al.*, 2006). *Régis Barillé* carries out reversible photostructurations of the surface of polymer films and biomaterials (Barillé *et al.*, 2010). *Stéphanie Leroy-Lhez* (thesis with *Frédéric Fages*, at Bordeaux) has functionalized fullerene C_{60} for photovoltaic conversion and synthesized new porphyrins for two-photon photodynamic therapy. She continues her research at the University of Limoges.

Le Mans (Université du Maine)

Laboratoire de physicochimie et photochimie organique

Pierre-François Casals studied, in particular, the photoaddition of β-diketones to diverse non-saturated systems (1970-1990).

Institut des Matériaux

Pascal Ruello, in cooperation with the "Ecole Centrale Paris", recently revealed the ultrafast and *"giant" photopiezoelectricity* of ferroelectric $BiFeO_3$ (Lejman *et al.*, 2014).

Orléans (University arbitrarily attached to the "Pays de la Loire")

Centre de recherche sur les solides imparfaits

Henri van Damme is known for his spectroscopic studies of adsorbed species on mineral colloids and clays, notably fluorescence decays.
Claude Hélène (*vide* Paris, MNHN) carried out research in this University (1974-1982), at the "Centre de Biophysique Moléculaire (Montenay-Garestier *et al.* 1976).

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Table A

Photochemical Associations

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

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

Theoreticians	Organic chemists	Physicochemists
- O. Chalvet (Paris)	- J.-J. Basselier (Paris)	- Mme A. Bernas (Orsay)
- R. Daudel (Paris)	- G. Beugelmans (Gif)	- J. Bourdon (Paris)
- C. R. Guerillot (Rennes)	- H. Bouas-Laurent (Bordeaux)	- Mme Dran (Lille)
- J. P. Malrieu (Paris)	- G. Cauquis (Grenoble)	- G. Emschwiller (Paris)
- L. Salem (Orsay)	- P. Courtot (Brest)	- P. Goudmand (Lille)
	- A. Lablache-Combier (Lille)	- Mlle Ivanoff (Orsay)
	- R. Lalande (Bordeaux)	- J. Joussot-Dubien (Bordeaux)
	-. J. Levisalles (Nancy)	- S. Leach (Orsay)
	- J. C. Mani (Montpellier)	- J. Lemaire (Nancy)
	- Mme E. Montaudon (Bordeaux)	- L. Lindqvist (Orsay)
	- Mme M. Mousseron-Canet (Mpellier)	- M. Niclause(Nancy)
	- M. Pfau (Paris)	- M. Poquet (Pau)
	- B. Pouyet (Lyon)	- J. L. Seris (Pau)
	- J. Rigaudy (Paris)	- Mme C. Vermeil (Paris)
	- G. Rio (Paris)	

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

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

d) Groupe Français de Cinétique et Photochimie (GFCP). Founded in 1980 by R. Lesclaux in order to bring together once a year specialists of combustion, gas phase kinetics, photochemistry and theoretical chemistry. The first meetings took place in Paris (ESPCI) and then in diverse French towns.
e) Société Française de Photobiologie (SFPb), E. Sage president since 2008.
f) European Society for Photobiology, (ESP), E. Sage president, 2011-2013.

Table B

Special Issues and Accounts in "l'Actualité Chimique"

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

Table C

BOOKS AND COLLECTIVE VOLUMES

a) « *Photochimie et Réactions Moléculaires* », Mousseron-Canet M., Mani J.-C., Dunod, Paris, 1969.
b) « *Eléments de Photochimie Avancée* », Courtot P. editor), Hermann Paris, 1972.
c) « *Photophysics and Photochemistry above 6 eV* », Lahmani F. (ed.), Elsevier, Amsterdam, 1985.
d) « *Photoinduced Electron Transfer* », Fox M. A., Chanon M., (eds), part B, Elsevier, 1988.
e) « *Handbook of Low Temperature Electronic Spectra of Polycyclic Aromatic Hydrocarbons* », Nakhimovsky L., Lamotte M., Joussot-Dubien J., Elsevier, 1989.
f) « *Lasers in Polymer Science and Technology: Applications* », Fouassier J.-P., Rabek J.F. (eds), CRC press, Boca Raton, 1990.
g) « *Laser Ablation of Electronic Materials: basic mechanisms and applications*" Fougarassy E., Lazare S. (eds), North Holland Amsterdam, 1992.
h) « *Photochromism: Molecules and Systems*", Dürr H., Bouas-Laurent H. (eds), Elsevier, Amsterdam, 1st edition 1990, 2nd edition 2003 (**1690** citations).
i) « *Technologie Photochimique ; Aspects Fondamentaux et Applications Industrielles de la Photochimie Préparative »,* Braun A., Maurette M. T., Oliveros E., Presses Polytechniques Romandes, Lausanne, 1986 (**1200** volumes sold). "*Photochemical Technology*", J. Wiley Chichester, 1991 (**2500** volumes sold).
j) « *Techniques d'Utilisation des Photons. Principes et Applications* », André J.-C., Vannes A. B. (eds), DOPEE85 Electra, 1992.
k) « *Radiation Curing in Polymer Science and Technology* », Fouassier J.-P., Rabek J. F. (eds), Chapman and Hall, Elsevier, London, 1993.
l) « *Photoinitiation, Photopolymerization and Photocuring. Fundamentals and Applications*», Fouassier J.-P., Hanser Gardner Publisher, Münich, 1995.
m) « *Homogeneous Photocatalysis* », Chanon M. (ed.), J. Wiley and sons, New York, 1997.
n) « *Organic Photochromic and Thermochromic Compounds* », Crano J.C., Guglielmetti R. (eds), vol. 1 and vol. 2, Plenum, New York, 1999, reprinted in 2006.

o) « *New Trends in Fluorescence Spectroscopy. Application to Chemical and Life Sciences* », Valeur B., Brochon J. -C., (eds), Springer-Verlag, Berlin, 2001.
p) « *Molecular Fluorescence. Principles and Applications* », Valeur B., Berberan-Santos M. N., Wiley-VCH, Weinheim, 1st edition 2001, 2nd edition 2012.
q) « *Lumière et Luminescence* », Valeur B., Belin ("pour la science"), Paris, 2005.
r) « *Réactions Ultrarapides en Solution ; Approches Expérimentales et Théoriques* », Mostafavi M., Gustavsson T., CNRS éditions, Paris, 2007.
s) « *Energy Dissipation in Molecular Systems* », Tramer A., Jungen C., Lahmani F., Springer, Berlin, 1st edition 2005, 2nd edition, 2010.
t) « *La Couleur dans tous ses Eclats* », Valeur B., Belin, Paris, 2011 (prize: "Le goût des sciences" 2011, prize : "Prisme" 2012, prize: "Roberval" 2013).
u) « *La Lumière et la Vie* », Valeur B., Bardez E., Belin, Paris, 2015.
v) "*Photocatalysis and Water Purification: From Fundamentals to Recent Applications*", P. Pichat (Ed.), Wiley-VCH, Weinheim, 2013.

Tableau D

Journals Editorial Boards

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

e) J. Fluorescence (Plenum). Associate editor: B. Valeur (Paris) 1995-1998 et 2002-2010.
f) J. Luminescence (Elsevier). Associate editor: C. Dujardin (Lyon).
g) J . Adv. Oxid. Technol. (Sci. Technol. Network); J. Environ. Sci. Health A (Taylor & Francis); Int. J. Photoenergy (Hindawi); Molecules (MDPI). Editorial committees : P. Pichat (Lyon).

Tableau E

Organization of International Conferences in France

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

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

Table F

French Contributions to IUPAC Technical Reports

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

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Acronyms

AFM : atomic force microscopy
Atochimie : Aquitaine Total Organico chemistry
CEA : Commissariat à l'Energie Atomique
CEISAM : Chimie et interdisciplinarité, Synthèse, Analyse, Modélisation
CGE: Compagnie Générale d'Electricité
CHU : Centre Hospitalier Universitaire
CIDNP : Chemically Induced Dynamic Nuclear Polarization
CMOA : Centre de Mécanique ondulatoire Appliquée
CNAM : Conservatoire des Arts et Métiers
CNEP : Centre National d'Evaluation de Photoprotection
CNET : Centre National d'Etudes des Télécommunications
CNRS : Centre National de la Recherche Scientifique
COMEX : Collisions Moléculaires en Milieux Extrêmes
CRPP : Centre de Recherches Paul Pascal
DICO: Dynamique et Interaction en Phase Condensée
DNA : Deoxyribonucleic acid
DSC : Differential Scanning Calorimetry
DSM : direction Scientifique de la matière (CEA)
EDF: Electricité De France
ENS : Ecole Normale Supérieure, rue d'Ulm Paris
ENSIC : Ecole Nationale Supérieure des Industries Chimiques
ENSSAT : Ecole Nationale Supérieure des Sciences Appliquées et de Technologie
ENSCP : Ecole Nationale Supérieure de Chimie de Paris, Paris-Tech
ENSCM : Ecole Nationale Supérieure de Chimie de Montpellier
EPA : European photochemistry Association
ESP : European Society for Photobiology
ESPCI : Ecole Supérieure de Physique et Chimie Industrielle, Paris
GDR : Groupe de Recherche (CNRS)

GFCP : Groupe Français de Cinétique et Photochimie
GFP : Groupe Français de Photochimie
GFP2P : Goupe Français de Photochimie, Photophysique et Photosciences
IBM : International Business Machines Corporation
ICMCB : Institut de Chimie de la Matière Condensée de Bordeaux
ICMMO : Institut de Chimie des Molécules et Matériaux d'Orsay
ICP: International Conference on Photochemistry
IMRCP : Laboratoire des Interactions Moléculaires et Réactivité Chimique et Photochimique
IMS : Intégration du Matériau au Système
INAC : Institut des Nanosciences et Cryogénie INSERM : Institut National de la Santé et de la Recherche Médicale
IR : Infrared
IRCEL : Institut de Recherche sur la Catalyse et l'Environnement de Lyon
ISIS : Institut de Science et d'Ingénierie Supramoléculaire
ISM : Institut des Sciences Moléculaires
IS2M : Institut de Sciences des Matériaux de Mulhouse
ISMO : Institut des Sciences Moléculaires
ISOP : International Symposium on Photochromism
ISyEB : Institut de Systématique, Evolution, Biodiversité
ITER : International Thermonuclear Experimental Reactor
ITODYS : Interfaces, Traitements, Organisation et Dynamique des Systèmes
IUPAC : International Union of Pure and Applied Chemistry
LASIR : Laboratoire de Spectroscopie Infrarouge et Raman
LCPO : Laboratoire de chimie des Polymères Organiques
LERMA : Laboratoire d'Etudes du Rayonnement et de la Matière en Astrophysique et Atmosphères
LERMAB : Laboratoire d'Etude et de Recherche sur le Matériau Bois
Lidyl : Laboratoire des interactions, dynamique et laser
LPTC : Laboratoire de Physico Toxicochimie des Systèmes Naturels
LPPM: Laboratory of Molecular Photophysics
LURE : Laboratoire pour l'utilisation du rayonnement électromagnétique
MNHN : Museum National d'Histoire Naturelle
NEO : Nanostructures Organiques
NIMBE: Nanosciences et Innovation pour les Matériaux, la Biomédecine, l'Energie

NLO: non linear optics
OLED : Organic Light ElectroLuminescent
NMR : Nuclear Magnetic Resonance
OPV : organic photovoltaic
PPG Industry : Pittsburgh Plate Glass, USA
PPS: Photochemical and Photobiological Sciences
PPSM : Laboratoire de Photophysique et de Photochimie Supramoléculaire et Macromoléculaire
RNA: ribonucleic acid
SFPb : French Society for Photobiology
SFPD : Société Française de PhotoDermatologie
SNPE : Société des Poudres et Explosifs
UCLA : University of California, Los Angeles
UPMC : Université Pierre et Marie Curie or Paris 6
V-UV : vacuum ultraviolet

List of Researchers

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

Adam Virgile : I, ESP
Amblard Jean : Orsay, ref. Belloni 1991, Mostafavi 1989
Amouyal Edmond: I, Orsay, Palaiseau, GFP2P, Aa, Bb,c, En, ref. 1995, Moradpour 1978
Angelié Christian : CEA Saclay
Anitoff Oleg: CEA Saclay
Attias André-Jean : Paris UPMC
Aubailly Michel : Paris MNHN
Audebert Pierre : Cachan ENS
Averbeck Dietrich : Orsay Institut Curie, ref. 1978, Dc
Baigl Damien : Paris ENS, ref. Venancio-Marques 2014, Anyfantakis 2014
Bailleux Christian : I, club EDF, ref. Ac, Ba
Banyasz Akos: CEA Saclay, ref. Gustavsson 2006
Bardez Elisabeth : Paris CNAM, ref. 1999, C u
Barillé Régis : Angers, ref. 2010
Barraud André : CEA Saclay

Bauer Edmond : Introduction I, Orsay
Bazin Marc : Paris MNHN
Becquerel Edmond : Introduction I, ref. 1839
Belloni Jacqueline : I, Orsay, ref. Bd, 1991, Mostafavi 1989
Bensasson René: Paris MNHN, Orsay, Bordeaux, ref. 1971, Amand 1975, Bonneau 1969, Moore 1984, Quaranta 2014, Seta 1985, D c.
Bernas Annette: Orsay, ref. 1972, Hautecloque 1985, A a
Berthelot Daniel: I, ref. 1910
Beswick Alberto: Orsay
Beugelmans René: Gif/Yvette, ref. 1979, 1979, TableA, a
Bigot Bernard: UPMC, ref. Devaquet 1978, Orsay
Blanchard-Desce Mireille: Rennes, Bordeaux, ref. 2013, 2015, Mongin 2002, Katan 2005, Genin 2014, Frochot 2015, Vaillant 2015
Bleuzen Anne: Orsay ICMMO, Bordeaux, ref. 2009
Boilot Jean-Pierre: Palaiseau, ref. Casanova 2007, Giaume 2008
Bonazzola Lydia : Orsay
Bonneau Stéphanie : Paris UPMC, ref. Mojzisova 2009
Bordage Amélie : Orsay ICMMO
Botter René : CEA Saclay, ref. Ripoche 1988
Bougon Roland : CEA Saclay
Boyé-Péronne Séverine : Orsay
Brault Daniel : Paris MNHN, UPMC ref. Mojzisova 2009
Brazard Johanna : CEA Saclay
Brohan Luc : Nantes, ref. Cottineau 2008
Bullot Jacques : Orsay
Carré Christiane : Brest, Mulhouse, ref. Ibrahim 2012
Casals Pierre-François : Le Mans
Cauchatier Michel : CEA Saclay
Cauchois Yvette : Orsay
Cauquis Georges : Paris, ESPCI, Grenoble, ref. 1967, Table A a
Chaquin Patrick : Paris UPMC, ref. 1977, 1990
Chalvet Odilon : Paris UPMC, ref. 1970, Bertrán 1969, Table A
Changenet-Barret Pascale : Paris ENS, Saclay CEA, ref. 1997, 2005
Chantzis Agisilaos : Nantes, ref. Kedong 2014
Che Michel : Paris UPMC, ref. Chizallet 2008
Clavier Gilles : Cachan, ref. Grazon 2013
Clerc Michel : CEA Saclay, ref. 1967, Alexandre 1983
Cordier Pierre : Orsay
Cossart Claudina : Orsay

Cossart Daniel : Orsay
Cossy Janine : Paris ESPCI, Reims, ref. Belotti 1985
Courtot Pierre : I, Paris ESPCI, Brest, ref. 1977, Tableau A, C b
Daguerre Jacques : I.
D'Angelo Jean : Paris UPMC, ref. 1983
Daniel Chantal : Nantes, Strasbourg, ref. 1984, Jacquemin 2014
Daudel Raymond : Paris UPMC, ref. 1967, Bertrán 1969, Chalvet 1970, Tableau A
Delaire Jacques : Orsay, Cachan, ref. 2000, D b
Derai Renée : Orsay
Desprès Alain : Orsay
Devaquet Alain : Paris UPMC, ref. 1978, Orsay
Dimicoli Iliana : CEA Saclay, ref. Ripoche 1988, Mons 1990
Doré Jean-François : I, SFPb, ref. Green 2006,
Douzou Pierre : Paris MNHN, 1961, ref. Bonfils 1979
Dujardin Gérald : Orsay, ref. 1983
Dufraisse Charles : I, ESCPI, Collège de France, ref. 1936
Dutuit Odile : Orsay
Duval Marie Christine : Orsay
Emschwiller Guy: I, Paris (ESCPI), ref., 1930, 1954, Job 1924, Tableau A
Evleth Earl M.: Paris UPMC, ref. Kassab 1983
Faucon Adrien : Nantes, ref. 2014
Fenistein Serge : Orsay, ref. 1990
Fichou Denis : Thiais, ref. 2000, Garnier 1990, Videlot 1999
Folcher Gérard : CEA Saclay
Fontaine-Aupart Marie-Pierre : Orsay, ref. Lévêque-Fort 2003
Fornasieri Giulia : Orsay ICMMO
Fortage Jérôme : Nantes, ref. 2008, Gibson 2009, Stoll 2014
Fournier Janine : Paris ESPCI, ref. 1999, Masanet 1973
Furth Bernard : Paris UPMC
Galaup Jean-Pierre : Orsay, ref. Rodriguez-Otazo 2009
Gallais Odile : Orsay
Garnier Francis : Thiais, ref. 1990, Videlot 1999
Gauduel Yann-Antoine : CEA Saclay, ref. 2001, B e
Gauthier Monique : Orsay, ref. Bernas 1972
Gauyacq Dolorès : Orsay
Gazeau Marie-Claire : Paris XII
Giannotti Charles : Gif-sur-Yvette, Montpellier, ref. Mérienne 1973, Lerner 1982

Girard Pierre-Marie : Orsay Institut Curie
Giusti Annick : Orsay
Govers Tom : Orsay
Grajcar Lydie : Orsay, ref. Leach 1959
Grand Dora : Orsay, ref. Bernas 1972, Hautecloque 1985
Guerchais Véronique : Nantes, Rennes, ref. Kedong 2014,
Guglielmetti Robert: Brest, Marseille, ref. Baillet 1993, Samat 2001, C n, E g
Guiard Bernard : Paris UPMC
Gustavsson Thomas : I, Orsay, CEA Saclay, ref. 1998, 2001, 2006, Markovitsi 2006, Markovitsi 2007, Vaya 2010, C r, F e
Hautecloque Simone : Orsay, ref. 1985
Hélène Claude : Paris MNHN, Orléans, ref. 1976,1987, Teulade-Fichou 2001, Montenay-Garestier 1976
Hellner Lucette : Paris ESCPI, ref. 1971
Heninger Michel : Orsay, Finistein 1990
Henri Victor: I
Herlin-Boime Nathalie : CEA Saclay, ref. Guillois 2004
Hickel Bernard : CEA Saclay
Horani Marcel : Orsay
Improta Roberto : CEA Saclay, ref. Gustavsson 2006
Ishow Eléna : Nantes, ref. Faucon 2014, Snell 2015,
Ivanoff Nina : Orsay, Table A a
Jacquemin Denis : Nantes, ref. 2014, Perrier 2012, Kedong 2014, Fihey 2015,
Jaraudias Jean : CEA Saclay
Job Paul: I
Joliot Pierre : Paris Collège de France, ref. 1969
Jouvet Christophe : Orsay
Jullien Ludovic : Paris ENS, ref. Gagey 2007, Gautier 2014
Jungen Christophe: Orsay, Cs
Kagan Henri : Orsay, ref. Moradpour 1978
Kellmann Arlette : Orsay, ref. 1967
Kessler John : Nantes, ref. Torndahl 2007
Kieffer Fernand : Orsay
Kossanyi Jean : I, Paris, UPMC, ESPCI, Thiais, ref. 1979, 2003, Chaquin 1977, Wintgens 1994, E a, e, f
Kraljic Ivan : Orsay
Lagugné-Labarthet François : Nantes, ref. Snell 2015

Lahmani Françoise : Orsay, ref. 1974, Le Barbu 2002, Seurre 2004, Cc,s
Lalo Christiane : Paris ESCPI
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B a, b, C o, p, q, t ,u, D e, E i, F d, e
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Functionalization of phosphorescent cyclometalated iridium(III) and platinum(II) complexes by main-group element moieties

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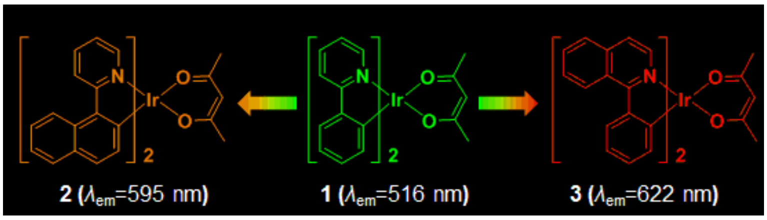
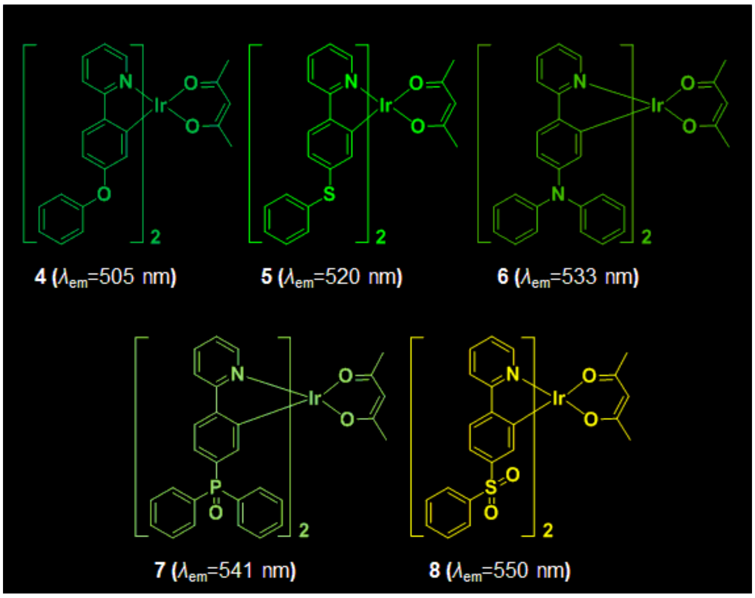
Phosphorescent cyclometalated iridium(III) and platinum(II) complexes have been widely used in organic light-emitting diodes (OLED) since they possess some inherent merits, such as readily tuning of emission colors, high electroluminescent efficiency, good electrochemical and thermal stabilities.[1, 2] Besides the stabilities, the emission colors and the electroluminescent efficiencies are the most concerned issues for cyclometalated iridium(III) and platinum(II) complexes when utilized as phosphorescent emitters in OLEDs which can show great potential in developing new-generation displays with fast response, ultra-thin thickness, wide view-angle and high-contrast features as well as energy-saving solid lighting sources. Therefore, the main goal in our researches is to adjust these the properties of cyclometalated iridium(III) and platinum(II) complexes to fulfill the requirement of their practical applications aforementioned.

As to cyclometalated iridium(III) complexes, their emission colors are very sensitive to their cyclometalating ligands. One can easily tune the emission color of an iridium(III) complex by just controlling the π-conjugation length of its ligand. As depicted in figure 1, fusing only one phenyl ring to the 2-phenylpydine (ppy) ligand, the emission maximum (λ_{em}) can be shifted from 516 nm for **1**[1] to ~595 nm for **2**[3] and 622 nm for **3**,[4] which means that it is very rough to tune the emission color by simply expanding or shortening the π-conjugation length of ligand.



2 (λ_{em}=595 nm) **1** (λ_{em}=516 nm) **3** (λ_{em}=622 nm)

Figure 1. Roughly tuning emission colors of iridium(III) complexes by controlling the π-conjugation lengths of their ligands.



4 (λ_{em}=505 nm) **5** (λ_{em}=520 nm) **6** (λ_{em}=533 nm)

7 (λ_{em}=541 nm) **8** (λ_{em}=550 nm)

Figure 2. Finely tuning emission colors of iridium(III) complexes with main-group functional substituents.

In order to finely tune the emission colors of iridium(III) complexes, we adopted a new tactic by incorporating main-group functional substituents into the cyclometalating ligands to synthesize a series of bis- and tris-cyclometalated iridium(III) complexes.5, 6 The main-group functional substituents were selected because they possess diverse electronic effects which can effectively adjust the highest occupied molecular orbital (HOMO) or the lowest unoccupied molecular orbital (LUMO) levels to different degree, and thereby tune the emissions to different color regions (4-8 in Figure 2).

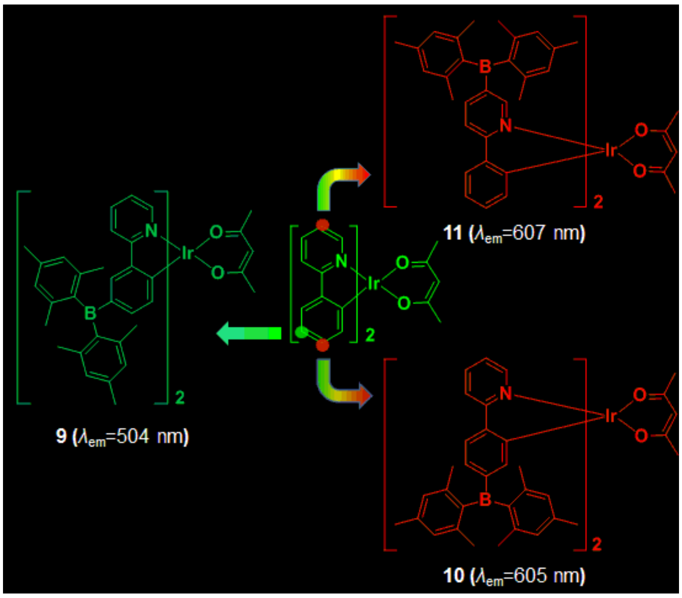


Figure 3. Tuning emission colors of iridium(III) complexes by altering the substituent positions on the ligands.

Besides the introduction of different main-group functional substituents to ligands, we also successfully tuned the emission colors by altering the substituent positions on the ppy ligand.7 As shown in figure 3, the dimesitylboron group located at the C5 position on the phenyl ring shows little effect on the emission color of 9 (λem=504 nm) compared to that of 1 (λem=516 nm), while the dimesitylboron group located at the C4 position on the phenyl ring or at the C5 position on the pyridyl ring can change the emission color from green for 1 to red for 10 (λem=605 nm) or 11 (λem=607 nm). This result indicates that the C5 position on the phenyl ring of the ppy ligand possesses higher electron density than the C4 position on the phenyl ring and the C5 position on the pyridyl ring, which could provide noteworthy guidance for effectively tuning the emission colors of iridium(III) complexes by introducing substituents to the ppy ligand.

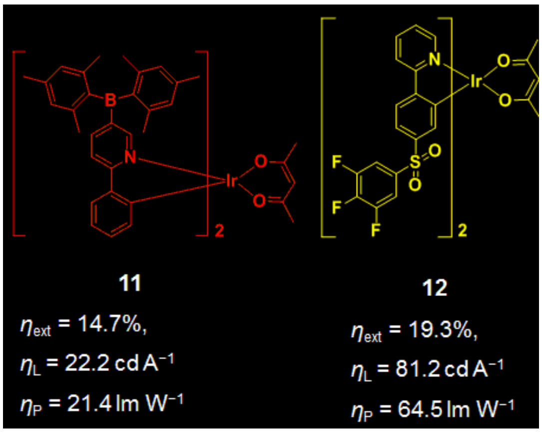


Figure 4. Improving electroluminescent efficiencies of iridium(III) complexes with main-group functional substituents.

Obviously, the main-group functional substituents are quite useful to finely tune the emission colors of cyclometalated iridium(III) complexes. Moreover, the main-group functional substituents can also play important roles in improving the electroluminescent efficiencies of cyclometalated iridium(III) complexes. For example (Figure 4), the red-emitting OLED using 11 as emitter shows high external quantum efficiency (ηext) of 14.7%, current efficiency (ηL) of 22.2 cd A−1, and power efficiency (ηP) of 21.4 lm W−1, and the yellow-emitting OLED based on 12 achieves ηext, ηL and ηP of 19.3%, 81.2 cd A−1 and 64.5 lm W−1, respectively.7, 8 Two main advantages may be credited for their high electroluminescent efficiencies. One is their extremely high photoluminescent yields up to nearly unity, the other is their improved electron injection/transporting ability. Unquestionably, these two advantages are conferred by the main-group functional substituents, i.e., dimesitylboron group and the fluorinated aromatic sulfonyl group, which have strong electron-withdrawing properties.

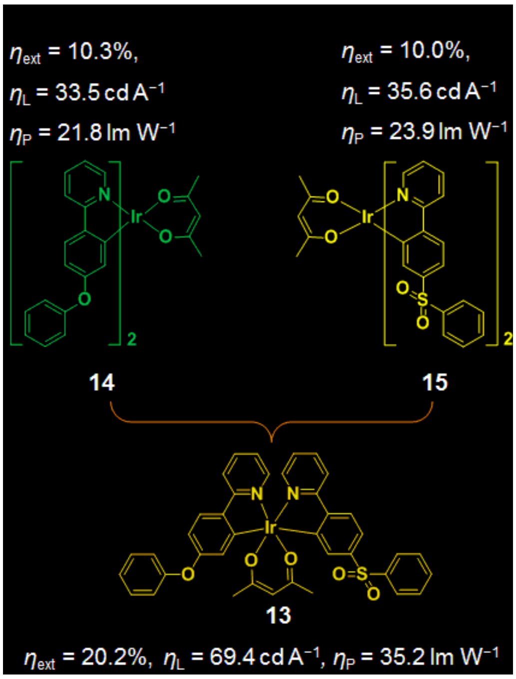


Figure 5. Improving electroluminescent efficiencies of iridium(III) complexes by designing asymmetric structures.

Actually, in order to improve the performance of OLEDs, it is better when the cyclometalated iridium(III) complexes show balanced hole and electron injection/transporting abilities. However, the cyclometalating ligands in one molecule are always identical for most of the cyclometalated iridium(III) complexes including those mentioned above, which means that the molecules can only show one dominating charge carrier injection/transporting ability. To solve this problem, we designed some iridium(III) complexes consisting of different cyclometalating ligands in one molecule.9, 10 The electron-rich phenoxyl group and the electron-withdraw sulfonyl group endow 13 with improved and balanced charge carrier injection/transporting ability so that the related OLED exhibits the ηext of 20.2%, ηL of 69.4 cd A−1 and ηP of 35.2 lm W−1.9 These electroluminescent efficiencies for 13 are much higher than those for 14 (10.3%, 33.5 cd A−1 and 21.8 lm W−1) and 15 (10.0%, 35.6 cd A−1 and 23.9 lm

W−1) with identical cyclometalating ligands in one molecule (Figure 5), indicating that it is a good strategy to improve the electroluminescent efficiencies of cyclometalated iridium(III) complexes by designing asymmetric structures containing cyclometalating ligands with different electron features.

Very recently, we have developed a novel way to tune the emission color as well as enhance the electroluminescent efficiencies of cyclometalated iridium(III) complexes. Different from previous researches which always design cyclometalated iridium(III) complexes only by manipulating the structures of ligands and thus obtaining an iridium(III) complex with only one metal center,[2] we successfully incorporated a second Ir center into an iridium(III) complex, leading to a dramatic optoelectronic property change of the iridium(III) complex.[11] As shown in figure 6, the emission color can be tuned from green for the mononuclear complex **16** (λ_{em}=526 nm) to red for the dinuclear complex **17** (λ_{em}=606 nm). Additionally, the electroluminescence investigations demonstrate that the solution-processed OLED based on **16** gives η_{ext}, η_L and η_P of 6.9%, 26.5 cd A^{-1} and 11.2 lm W^{-1}, respectively, while the OLED based on **17** with the same device structure displays an impressive performance with η_{ext}, η_L and η_P greatly improved to 14.4%, 27.2 cd A^{-1} and 19.5 lm W^{-1}, respectively. The almost 100% η_{ext} and η_P enhancements from the OLED based on **16** to the OLED based **17** mainly origin from the improved and balanced charge carrier injection/transporting ability of **17**. This study shows that the introduction of a second Ir center to the cyclometalated iridium(III) complex is a novel tactics to remarkably tune the emission color as well as enhance the electroluminescent efficiencies, which has provided us a new research direction on developing high performance cyclometalated iridium(III) complexes.

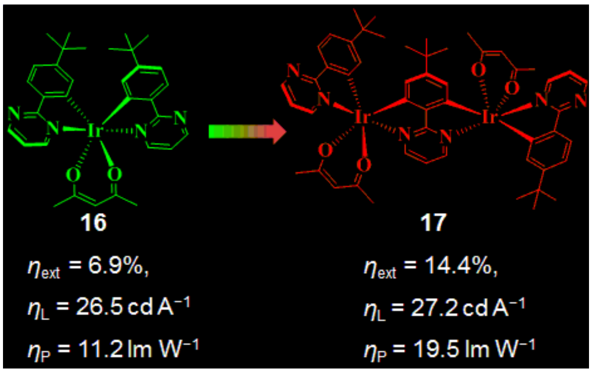


Figure 6. Improving electroluminescent efficiencies of iridium(III) complexes by introducing a second Ir center.

Different from their monochromic analogous, white light-emitting diodes (WOLEDs) can give broad electroluminescent spectra for lighting purpose. As an ideal candidate for lighting sources, WOLEDs should possess the features of high EL efficiencies and color rendering index (CRI) higher than 85 at least. By employing diphenylamino functionalized cyclometalated iridium(III) complexe **18** (Figure 7),[12] the solution-processed WOLEDs can show very high electroluminescent efficiencies with η_{ext}, η_L and η_P of 19.1%, 42.9 cd A^{-1} and 20.3 lm W^{-1}, representing the first solution-processed WOLED which can exceeds the efficiency of incandescent light bulbs. This result paves the road to low-cost and large-area polymer-based WOLEDs for solid-state lighting. In addition, cyclometalated platiinum(II) complexes **19** and **20** functionalized with main-group moieties have also been prepared to make WOLEDs.[13] Importantly, the WOLEDs with single emission layer can produce white light possessing exceptional quality with CIR of 97, Commisssion Internationale de L'Eclairage (CIE) coordinates of (0.320,0.340) and correlated color temperature (CCT) of 6066 K (Figure 7). All these results can provide important information for developing WOLEDs as practical lighting sources.

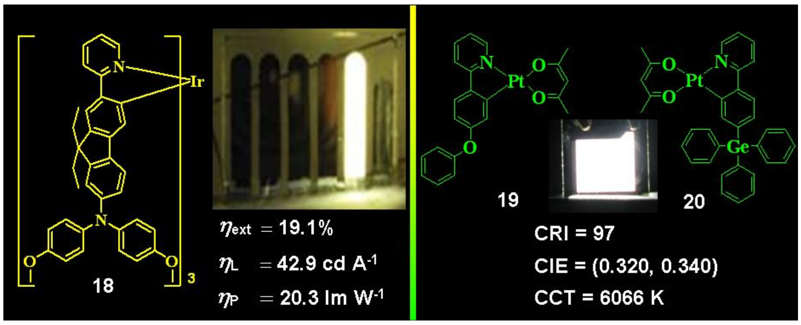


Figure 7. High performance WOLEDs based on functionalized iridium(III) and platinum(II) complexes bearing main-group element moieties.

In brief, main-group functional substituents are versatile blocks for tuning the emission colors and improving the electroluminescent efficiencies of cyclometalated iridium(III) and platinum(II) complexes, which can show great potential in developing both new-generation displays and future energy-saving lighting sources.

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SPECIAL REPORTS ON SUNLIGHT PHOTOCATALYSIS

Introduction

Dear EPA members,

The EPA Newsletter (June 2016) is dedicated to "Sunlight Photocatalysis", and experts in this area of research show here that this topic is currently a vital research area.

Researchers from different countries have provided contributions on their activity in this area. In this issue, *Hermegildo Garcia (Polytechnic University of Valencia)* reports on the possible roles of Au in TiO_2/Au photocatalysis and discusses on parameters to be controlled to increase the efficiency of systems consisting of Au nanoparticles supported on TiO_2 in sunlight induced processes. *Juan C. Scaiano et al. (University of Ottawa)* report on a strategy to makes easier the proper characterization of chain propagation in visible light photoredox catalysis. *Petr Kluson et al. (Institute of Chemical Process Fundamentals Academy of Sciences of the Czech Republic)* inform on the simulation of sunlight conditions in ultraviolet driven heterogeneous photocatalytic oxidations. *Jincai Zhao et al. (Chinese Academy of Sciences, Beijing)* report on the relevant role of proton-electron transfer processes in the water oxidation on hematite. *Maurizio Fagnoni et al. (University of Pavia)* account on the interest of decatungstate salts as the relevant photocatalyst in organic synthesis fulfilling most of the green chemistry principles. *Raúl Pérez-Ruiz (University of Regensburg)* reports on current research being carried out in *Axel Jacobi von Wangelin* group related to a suitable strategy to activate aryl halides using a metal-free strategy based on visible-to-ultraviolet photon upconversion by triplet-triplet annihilation. *Horst Kish (University of Erlangen-Nürnberg)* informs on the redox activation of small molecules under visible light by using simple inorganic semiconductors and photosensitizers.

As always, we wholeheartedly thank all the contributors for their specialized reports on *sunlight photocatalysis* which are the proof of the effort made by experts in this field. There is still much research work to be done in this area and these contributions show us how alert we must be to find smart new strategies to boost the use of sunlight for sustainable development.

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Dual role of Au nanoparticles as co-catalysts and visible light harvesters in the photocatalytic hydrogen generation by Au/TiO_2 photocatalyst

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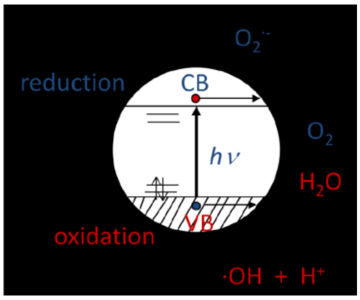
Abstract.

After presenting the limitation of TiO_2 as photocatalyst for hydrogen generation and the possible alternatives to overcome this problem, this manuscript focus on the use of Au nanoparticles to promote visible light photocatalytic activity commenting the reasons of stability of the material and emphasizing its reliable preparation. The possible roles of Au depending on whether excitation occurs at TiO_2 or at the visible plasmon band are commented as well as the influence of particle size and alloying in terms of activity and selectivity. The final part discusses open issues to further improve the efficiency based on the use of TiO_2 supported Au nanoparticles, particularly understanding the mechanism of photosensitization and which are the most appropriate morphology, size distribution and grafting procedure to deposit Au nanoparticles on TiO_2 .

General strategies to introduce visible light photoresponse on TiO_2.

In the context of the use of solar light as primary energy resource, there is much interest in developing photocatalysts that can efficiently utilize sunlight to prepare chemicals that can be employed as transportation fuels.[1-3] Among the most general and studied photocatalysts, titanium dioxide and several other metal oxides can exhibit high photocatalytic activity under UV irradiation. [4-7] TiO_2 in the anatase form is a UV responsive semiconductor with a gap energy value of 3.2 eV, corresponding to the onset of its absorption band to about 380 nm in the UV region. To act as photocatalysts, semiconductors must absorb photons whose energy is larger than the bandgap of the material, resulting in the generation of a charge separate state with the promotion of one electron from the valence to the conduction band. In the case of TiO_2 in the anatase phase, only radiations of wavelength shorter than 380 nm are absorbed. Unfortunately, the percentage of solar energy reaching the Earth surface corresponding to UV radiation is about 4%, while the proportion of visible light is 42% and the rest corresponds to IR wavelengths. Therefore, in order to increase the efficiency of a photocatalyst, in particular TiO_2, under solar light irradiation, it is necessary to modify the material to expand its photoresponse into the visible and, hopefully, also in the near IR zone.

Four general approaches have been reported to increase the photocatalytic efficiency of TiO_2 to visible light, including metal doping, doping with non-metallic elements and the generation of oxygen vacancies, amorphization of the outermost external layers and photosensitization.[4-8] Doping, either with metallic or non-metallic elements, introduces in the band gap space additional orbitals, either empty (case of metals) or full (case of non-metallic elements) of electrons, resulting in the effective shortening of the band gap. Scheme 1 illustrates the presence of intra band gap states by the presence of dopant atoms.



Scheme 1. Illustration showing the influence of metal doping (empty orbitals below the conduction band, CB) or non-metal doping (full orbitals above the valence band, VB) with indication of how under ambient conditions CB electrons react with molecular oxygen and VB holes are trapped by ambient moisture.

Doping is, however, not a fully satisfactory strategy to diminish the band gap energy, mainly due to its robustness and lattice stability of TiO_2 crystallographic phases. The large stability of TiO_2 crystal frameworks disfavors the presence of an heteroatom in a stable way and, over prolonged operation periods, these dopant elements are expelled out of the lattice. Two options, either synthesis of TiO_2 in the presence of the dopant element or modification of preformed TiO_2 , can be used in principle for doping. Doping during preparation of TiO_2 is based on solid-gel synthesis recipes that encounter the general problem that amorphous solids of low photocatalytic activity are initially obtained. A calcination treatment is necessary to convert the amorphous TiO_2 into highly crystalline materials with low defect density and higher charge carrier mobility. But this calcination step healing defects has as obvious consequence a considerable decrease in the percentage of the doping element that remains in the TiO_2 lattice, expelling most of the dopant element out of the TiO_2 crystallite as a separate phase. Similarly, post-modification of the robust TiO_2 framework is difficult and requires high temperatures, making uncertain the loading of the dopant element that has been introduced in the lattice. Post-synthetic modification of TiO_2 powders by treatment of with NH_3 at high temperatures is one of the preferred methods for N-doping, but it is clear that this procedure should mostly graft N atoms on the external surface of the particles and it is difficult to accept that this treatment can lead to a uniform doping of N-atoms throughout the particle. Furthermore, high-temperature treatments with reduced agents such as NH_3 can also result in the creation of O atoms vacancies that also influence the bandgap energy.

Black TiO_2 obtained by submitting preformed TiO_2 crystals to harsh reduction treatments, for instance submitting the solid to temperatures above 300 ^{o}C under H_2 or using a metal hydride as reducing agent renders a material characterized by its gray or black color that sharply contrasts with the white appearance of TiO_2 . It has been proposed that these visual changes derives from the alteration of the surface and subsurface composition of TiO_2 nanoparticles during the reductive treatment that leads to the creation of oxygen atom vacancies and an increase in the defects on this layer. Black TiO_2 has been reported to exhibit visible light photocatalytic activity for H_2 generation from H_2O in the presence of sacrificial electron donors, but the reproducibility of the results and the stability of black titania are matters of concern.[9] In addition, black TiO_2 still requires Pt as co-catalyst to increase the efficiency in H_2 evolution.[10, 11]

Besides lack of reproducibility and difficulty in characterization, another concern of doping and surface amorphization is the poor stability of the material upon extensive use as photocatalysts due to photocorrosion that leads to leaching of the dopant element and healing of the oxygen vacancies. Since the dopant element and defects are involved in the process of charge separation and recombination, consecutive cycling with the corresponding swinging in the oxidation state of the dopant element may result in a continued stress resulting in the corrosion and migration of the element to extra framework positions.

Photosensitization upon excitation of metal nanoparticles

An alternative to doping that has also been shown to introduce visible light photoresponse is photosensitization. In this strategy there is a light harvester unit attached to the semiconductor surface that absorbs light and injects one electron to the conduction band of the semiconductor, such as TiO_2 . Dyes, either metallic complexes or organic molecules, are general visible light harvesters and this strategy has proven to be useful in the construction of dye sensitized solar cells.[12-15] However, for photocatalytic applications it is generally considered that organic dyes or metallic complexes are not sufficiently robust and they would decompose during operation.

One alternative to introduce visible light photoresponse in TiO_2 and other wide bandgap semiconductors are metal nanoparticles (NPs) exhibiting plasmon absorption band in the visible region such as Au, Ag and Cu. Among them, Au is the preferred one due to its large stability against oxidation, resulting in highly stable Au NPs adsorbed on the surface of the semiconductor, particularly TiO_2 .

Among the possible ways to deposit Au NPs supported on TiO_2 NPs, Haruta reported in the 80s a method denoted as deposition-precipitation that is highly reproducible in forming Au NPs of narrow particle size distribution centred about 5 nm for Au loadings below a few percents on TiO_2 .[16, 17] Figure 1 shows a TEM image of a Au/TiO_2 sample in which the Au NP particle size distribution is shown. This Au/TiO_2 material exhibits catalytic activity for a wide range of reactions including low-temperature CO oxidation, selective hydrogenations, aerobic oxidations and epoxide rearrangement among others.[18, 19]

Due to the presence of Au NPs, Au/TiO_2 exhibits a characteristic pink color with two absorption bands, one in the UV at λmax about 320 nm corresponding to TiO_2 and other, less intense due to the low Au percentage, in the visible region with λmax about 620 nm corresponding to the plasmon band of Au. The relative intensity of this visible band increases with Au loading. Figure 1 also shows characteristic UV-Vis absorption spectra of Au/TiO_2 in where the presence of the plasmon band in the visible region responsible for the dark pink color of the sample can be observed.

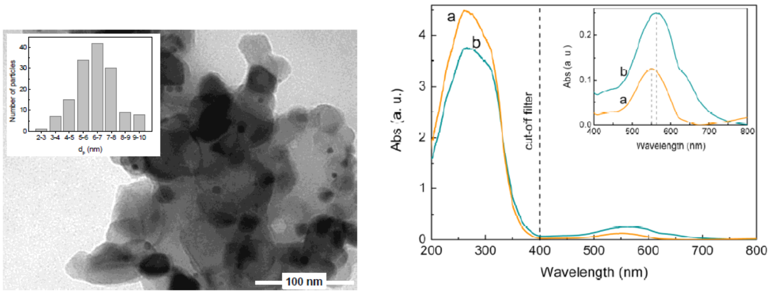


Figure 1. Left: TEM image of Au/TiO_2 prepared by the deposition precipitation method and having 0.5 wt.% Au. The inset shows the histogram of Au particle size distribution. Right: Optical diffuse reflectance UV-Vis absorption spectra of two Au/TiO_2 samples having 0.2 and 0.5 wt.% Au loading and indication of the cut off wavelength of UV filters. The inset shows an expansion of Au plasmon band.

Not surprisingly in view of the UV photocatalytic activity of TiO_2 , Au/TiO_2 has also photocatalytic activity in the UV that is enhanced due to the presence of Au. Pt and other noble metals such as Ir or Pd are widely used as co-catalysts to increase the photocatalytic activity of TiO_2 in the UV, for instance for H_2 generation from aqueous solutions containing sacrificial electron donors such as alcohols or amines. In one of the pioneering studies, Haruta also compared the photocatalytic activity of Au/TiO_2 respect to Pt/TiO_2 upon UV-Vis irradiation and concluded that the role of Au is similar, although with lower efficiency, to that of Pt for H_2 generation.[20]

However, in contrast to Pt that does not exhibit visible absorption band, Au NPs due to their visible plasmon band have been found to introduce photocatalytic TiO_2 response for hydrogen generation from water-methanol mixtures under visible light irradiation.[21] Optimization of the visible light photocatalytic activity as a function of the Au loading has shown that the maximal efficiency is obtained for the range between 0.2 to 2 wt%, there being necessary only a minute amount of Au NPs to reach the highest activity.[21] The photo-action spectrum in the visible region for Au/TiO_2 as photocatalyst for hydrogen generation agrees well with the visible plasmon band of Au NPs supporting the assignment of Au NPs as those responsible for light absorption in this spectral range. As an example, Figure 2 shows the photocatalytic hydrogen generation using monochromatic 532 nm light for TiO_2 and Au/TiO_2 showing the contrasting behavior between the two materials. Thus, Au/TiO_2 combines several advantages that make this material a convenient visible light photocatalyst including reliable and reproducible preparation method based on the deposition-precipitation protocol, high stability due to the noble character of Au and the fact that this metal is not doping robust TiO_2 and visible light photocatalytic activity for just minute Au loadings.

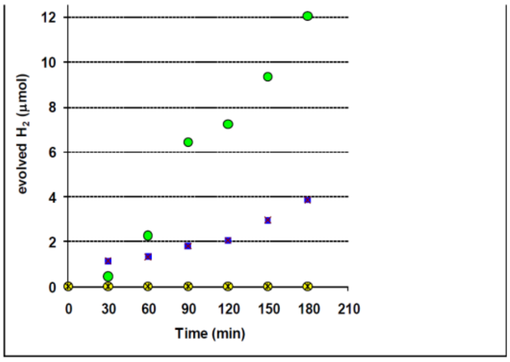
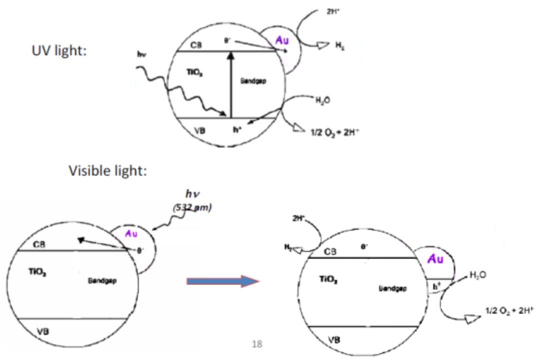


Figure 2. Photocatalytic activity for hydrogen generation upon 532 nm laser excitation (green dots) or similated sunlight irradiation (blue squares) of Au/TiO_2 compared to the response of TiO_2 irradiation with a laser at 532 nm (yellow dots).

The same effect of the presence of Au NPs on TiO2 for the photocatalytic hydrogen generation has also been demonstrated for CeO2 as photocatalyst for oxygen generation from water in the presence of Ag+ as electron acceptor agent.[22] The visible light photocatalytic activity of Au/CeO2 for oxygen generation under visible light irradiation was also optimized with respect to Au loading and only a minute amount of Au is needed to achieve the highest activity.

The fact that there is an optimal Au loading indicates that the presence of Au causes two opposite effects. In this regard, one interesting issue concerning the possible roles of Au NPs is the influence of particle size on the photocatalytic activity of semiconductors as a function of the excitation wavelength. By preparing a set of Au/TiO_2 samples with exactly the same Au loading but different particles sizes, a contrasting influence of the average particle size as a function of the irradiation wavelength was observed.[23] These Au/TiO_2 samples were prepared starting from a parent Au/TiO_2 sample that was submitted to annealing at increasing temperatures in the range from 200 to 400 ^{o}C. It is well known in the literature that thermal treatment of supported Au NPs increases the particle size due to the agglomeration of small Au NPs. This increase in the average particle size is generally an unwanted process in catalysis, due to the lower activity of larger Au NPs, but occurs when reactivating deactivated catalysts. Accordingly, under UV light, the photocatalytic activity of Au/TiO_2 samples decreases along the particle size. However, surprisingly under visible light illumination the smallest particle size is less active. This different photocatalytic performance as a function of the average Au particle size has been rationalized assuming a different role of Au NPs depending on whether excitation takes place directly at the semiconductor (UV) or at the Au NPs (visible). When TiO_2 is directly excited, then Au acts mostly as co-catalyst for hydrogen generation and this activity requires particles as small as possible. As commented, the decrease in the catalytic activity as the particle size of Au increases is a general observation, well known in heterogeneous catalysis that derives from the percentage of Au atoms that are located on the external surface. This percentage decreases exponentially as the diameter of NPs increases and internal Au atoms cannot interact with substrate. In contrast, when irradiation is carried out under visible light, it appears that one of the prevalent roles of Au NPs is as light harvester injecting electrons on the semiconductor and, under these conditions, the correlation of light absorption and photocatalytic activity is more important. Scheme 2 illustrates the two different situations depending on whether it is TiO_2 or Au NPs the component that absorbs light.

Note in this Scheme 2 the different location of electrons and holes that should have consequence on the reduction and oxidation potential of the photogenerated charge carriers.



Scheme 2. Comparison of the different locations of electrons and holes upon selective excitation of Au/TiO_2 either in the UV or with visible light.

Further support to this dual role of Au depending on the irradiation wavelength range was obtained by determining the influence that the presence of Pt forming alloy NPs with Au plays on the photocatalytic activity of $(Au,Pt)/TiO_2$. $(Au,Pt)/TiO_2$ is an interesting material because it could optimize the catalytic activity for hydrogen generation due to the presence of Pt with the visible light photoresponse introduced by Au NPs. A series of $(Au,Pt)/TiO_2$ samples having the same total metal content, but differing in the Au/Pt atomic ratio were prepared.[24] As the percentage of Pt increases in the alloy, the characteristic plasmon band of Au NPs diminishes in intensity and it absent for the Pt/TiO_2 .[24] Using visible light irradiation, it was observed that the performance of the set or five different samples for hydrogen generation from water in the presence of methanol as sacrificial electron donor was very similar. However, when an amine was used as sacrificial electron donor, then, the presence of Pt decreases the visible light photocatalytic activity. This decrease was interpreted as reflecting the decrease in the intensity of the visible light absorption band due to Au. It seems that when the sacrificial agent is a good electron donor, the catalytic activity of Pt that is better than that of Au has lower importance and the prevalent effect is visible light absorption. Overall, this study shows that there is no advantage on the presence of Pt as co-catalyst with respect to the visible-light photocatalytic activity of TiO_2 .

A similar study forming Au-Cu alloys modifying the photocatalytic activity of TiO_2 for visible light reduction of CO_2 has led to interesting results that give hints about the dual activity of metal NPs as co-catalysts and light harvesters.[25] It was observed that while Au/TiO_2 generates hydrogen from water regardless the presence or absence of CO_2, the introduction of Cu changes the selectivity of the process towards CO_2 reduction affording CH_4, without having a negative effect in the visible light photoresponse due to Au.[25] Thus, in optimal atomic proportions, the combination of Au and Cu forming alloy NPs on the surface of P25 TiO_2 can introduce visible light photoresponse and selectivity due to the combined action of both metals, each of them having a different role. Although, still not understood, transient spectroscopy has shown that the transient spectra of charge separation is quenched by CO_2 in the long wavelength region only when Cu is present in the composition of the photocatalyst.[26] This indicates that Cu is key for the interaction of the photogenerated charge separate state and CO_2 that does not occur when Cu is absent.

Efficiency of visible light photosensitization of TiO_2 by Au NPs.

It has to be commented, however, that the efficiency of hydrogen generation under UV light is much higher than that under visible light, where the quantum yield is lower. The photoaction spectrum for hydrogen generation from water in the presence of methanol by Au/TiO_2 is shown in Figure 3. As it can be seen there, the visible light efficiency is significantly lower than that in the UV due to the change in the component absorbing light. Furthermore, the same Au/TiO_2 sample as a thin micrometric film exhibits an enhanced UV photoresponse compared to TiO_2 , but does not have measurable photocurrent under visible light irradiation.

This contrasting presence or absence of visible light photoresponse of Au/TiO_2 for hydrogen generation or photocurrent has been explained based on the need of interparticle charge migration through micrometric distances in the case of photocurrent, while this interparticle migration is not needed in the case of hydrogen generation, where upon charge separation and diffusion of charge carriers to the particle surface, they will be quenched by substrates in contact with the particles.[27]

Transient spectroscopy allows monitoring the absorption spectra of the semiconductor upon charge separation. By following the temporal evolution of the signal, it is possible to determine the lifetimes and the proportion of the initial population of charge carriers that survive at different time scales. Majima, Fujitsuka and coworkers have studied the ultrafast response of Au/TiO_2 and observed that about 20% of the signal detect in the picoseconds time scale, survives beyond nanoseconds.[28] They also measured that some of the charge carriers can even live milliseconds after generation.[28] We have determined that the residual population of charge carriers reaching microseconds can be quenched in part by methanol and oxygen.[27] This incomplete quenching has been interpreted assuming that some charge carriers are trapped in sites inside the particle and they are not accessible to the quenchers. Only those charge carriers reaching the particle surface will be able to react with the quenchers. It is clear that understanding photocatalytic processes requires the combination of a series of techniques besides measurement of the photocatalytic activity under various conditions and photoaction spectra.

Transient spectroscopy, particularly in the more relevant microsecond time scale in which quenching phenomena take place, provides very important information about how Au NPs and their possible alloys can influence the photoresponse of TiO_2 . The first relevant data is that, while no transients are detected for TiO_2 , deposition of minute amounts of Au NPs in less than 1 wt.% is sufficient to detect a strong transient signal of charge carriers upon visible light excitation, thus, in agreement with the photocatalytic data. The key point in the current state of the art is how to enhance even further this visible light photoresponse. This is important when sunlight is used as light source, since the small proportion of UV light (about 4% of the total energy) can be responsible for a large percentage of the observed photocatalytic activity [27] and further increases in photocatalytic efficiency should arise from increasing the visible or even NIR activity. Thus, there is still room for improving the photocatalytic performance by increasing the efficiency of photosensitization by Au NPs. This has to be achieved by gaining understanding of the physical phenomena behind photosensitization by Au NPs. The plasmon band corresponds to the collective excitation of valence electrons of the metal in a confined space defined by the NP dimensions. Light excitation of the plasmon band is known to eject electrons from the metal NP to the surroundings.[29] However, theory indicates that the energy of these thermalized electrons could not have sufficient energy to be injected into the conduction band of the semiconductor. It has to be, however, commented that the conduction band energy of TiO_2 is not high compared to other semiconductors and in this regard the situation is not very unfavorable.

One possibility to increase the energy of electrons from Au NPs is reducing even further their dimensions to the point in where a transition from the metallic properties to molecular properties of Au takes place. The occurrence of discrete energy levels on small Au clusters would increase the LUMO energy and would make electron injection to TiO_2 conduction band thermodynamically more favorable. This reduction of Au particle size has to be compatible with minor possible variations in the intensity and position of the visible band of Au NPs. A compromise should be reached in such a way that optimization at atomic level of the number of Au atoms of the NPs and their geometry would enhance charge injection without paying much penalty on visible light absorption.

Another aspect to be considering is the kinetics of charge injection from Au NPs to TiO_2 conduction band trying to increase the efficiency of the process. This requires surely an adequate grafting and deposition of Au NPs on TiO_2 surface making the tunneling of electrons faster and with the minimum barrier. This could be, in principle, achieved by preparing TiO_2 particles with the adequate facets on which Au NPs should be deposited making the crossing of the surface between the two components easier by adequate orbital overlapping. This strategy has been successfully applied to dye photosensitization of TiO_2 and should also be possible in the present case.

Conclusions.

The ability of Au NPs in low weight percentages to introduce visible light photoresponse for hydrogen generation and CO_2 reduction is by now well documented. The stability of the TiO_2 photocatalyst containing Au NPs derives from the combination of the stability of both components and the strong grafting between them that has been well proven in heterogeneous catalysis in multitude of reactions and conditions and that also includes exposure of the material to light. The present data shows that the visible light activity derives from the plasmon absorption band of Au NPs that upon excitation injects electrons into TiO_2 conduction band. However, the lack of control at atomic level the size of Au NPs and their grafting on TiO_2 is limiting the preparation of the materials to samples where the average particle size distribution could not be the optimal for the photocatalytic process. Specifically it would be important to determine which percentage of electrons ejected from Au NPs are able to populate the conduction band of the semiconductor and how this percentage can be increased by control of Au NP geometry, number of atoms and grafting on TiO_2 particles. If this is achieved, then, it is likely that a robust and durable photocatalyst with high enough performance to allow development of a commercial process would be obtained. The final target in this area is to reach efficiencies and productivity high enough to compete with other alternative processes, particularly electrochemical ones, in the production of solar fuels.

Acknowledgements.

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Visible Light Redox Activation of Small Molecules by Semiconductor Photocatalysis

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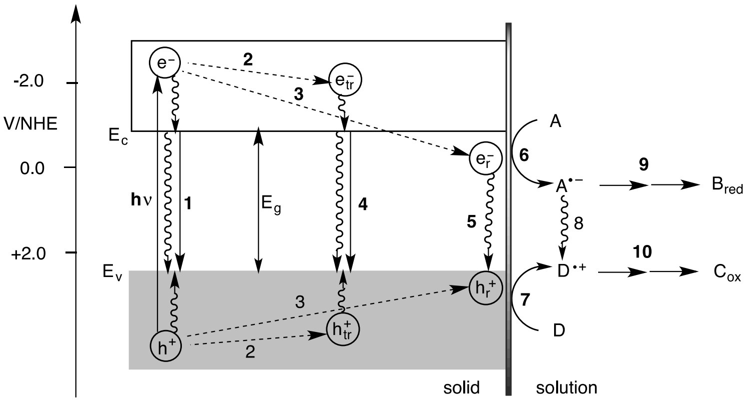
Photosynthesis of green plants constitutes the basis of human life. In this fantastic chemical process the chloroplast membrane acts as a heterogeneous, visible light active photosensitizer. From the point of photochemistry the reaction course may be broken down into four steps.

A) Photochemical charge separation.
B) Charge trapping at photosystem I and II (PS I and PS II).
C) Interfacial electron transfer (IFET) with NADP$^+$ at PS I and with H_2O at PS II.
D) Conversion of the primary redox products to oxygen and carbohydrates via CO_2 reduction
and H_2O oxidation through C-C- und O-O-bond formation, respectively.

Both in photosynthesis and artificial systems of chemical solar energy utilization the first two steps are of basic importance for the conversion of light into chemical energy. Different from homogeneous photosensitizers wherein charge recombination is too fast to allow concerted reduction and oxidation reactions, it is slow enough in heterogeneous semiconductor systems to enable charge trapping and subsequent concerted reductive and oxidative IFET reactions.[1] Scheme 1 summarizes the elementary processes occurring upon irradiation of a semiconductor crystal in contact with a solution of donor and acceptor substrates.[2] Light absorption generates an electron-hole pair (exciton), which undergoes in general a fast dissociation into the separated charges (polaron).[3] These may recombine (Scheme 1, step 1) or being trapped at unreactive and reactive (Scheme 1, steps 2, 3) surface centers. Although a differentiation between these states may be possible by quenching experiments, theses were very rarely conducted. In competition with charge recombination (Scheme 1, step 5) the reactive charges e_r^- and h_r^+ can undergo the IFET (Scheme 1, steps 6, 7) only when their reduction potentials are above and below those of A and D, respectively.[4]Noteworthy are the strongly positive E_v positions of titanium and tungsten oxide of 2.7 V and 2.9 V resulting in a high oxidation power of the photogenerated holes. The moderate reduction potentials of the corresponding electrons are -0.5 V and +0.1 V for TiO_2 and WO_3, respectively. The latter values become more negative and the former more positive as indicated by the band edge potentials of CdS (-0.9 V and +1.5 V) and ZnS (-1.8 V and +1.8 V).



Scheme 1. Simplified summary of elementary processes occurring upon light absorption by a semiconductor single crystal in contact with donor D and acceptor A (*Direct Semiconductor Photocatalysis*)[5] E_g, E_v and E_c correspond to bandgap and valence and conduction band edges, respectively. Values of E_g and E_v apply for titania in contact with neutral water. The vertical bar symbolizes the solid/solution phase boundary. Full and wavy lines correspond to radiative and nonradiative processes, dashed lines to charge trapping

In competition with back electron transfer (BET) the primary redox products A.- und D.+ generated in the IFET (Scheme 1, steps 6,7) are successively transformed into products Bred und Cox. Thus, the over-all reaction resembles steps A to C of photosynthesis and most semiconductor catalyzed (sensitized) photoreactions follow this scheme. The net reaction corresponds to "photoelectrolysis" since photogenerated charges induce formation of reduced and oxidized products. We have proposed to classify this major reaction type as Semiconductor Photocatalysis Type A (Eq.1, SC = semiconductor). In a very few cases the primary redox products undergo intermolecular bond formation affording an addition product (Semiconductor Photocatalysis Type B, Eq.2). In the following we briefly summarize selected results of our work, which illustrate the power of semiconductor photocatalysis for molecular redox activation driven by visible light.

$$\mathrm{A} + \mathrm{D} \xrightarrow[\mathrm{SC}]{h\nu} \mathrm{B}_{\mathrm{red}} + \mathrm{C}_{\mathrm{ox}} \qquad (1)$$

$$\mathrm{A} + \mathrm{D} \xrightarrow[\mathrm{SC}]{h\nu} \mathrm{A{-}D} \qquad (2)$$

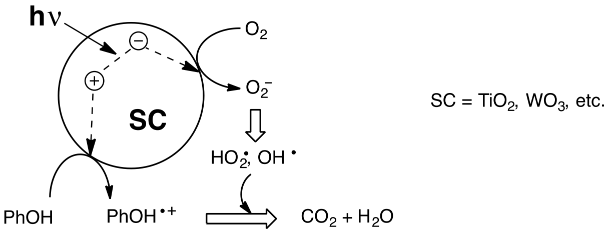
Semiconductor Type A Photocatalysis

Aerobic Oxidation

Besides the cleavage of water into hydrogen and oxygen, the holy grail of photocatalysis[6,7], Carbon dioxide reduction to C_1 and C_2 products[8], the exhaustive oxidation of pollutants in air and water was in the focus of most investigations.[9] In such reactions aerial oxygen is reduced to reactive oxygen compounds in the reactive IFET (Scheme 2). The pollutant radical cations formed in the oxidative IFET are in general finally completely oxidized. This field has reached technical application in the form of photoactive surfaces, especially dispersion paints.[10-12]

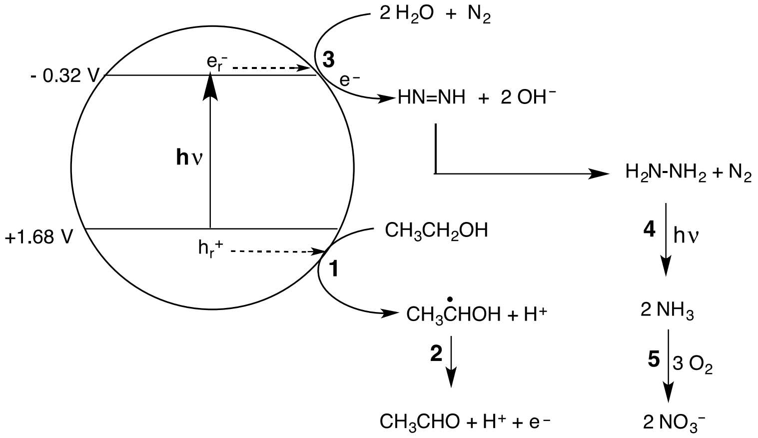
N_2-Fixation

Next to photosynthesis nitrogen fixation is the second most important process of the biosphere. Stimulated by the pioneering work of Schrauzer on the iron-doped rutile (0.2 % Fe3+) photocatalyzed UV reduction of dinitrogen by water to ammonia (about 6 □ mol)13, we prepared thin films (300 nm thick) of iron titanates by dip-coating of glass slides with ethanolic mixtures of Ti(OEt)4 and anhydrous FeCl3, followed by annealing at 600 °C.



Scheme 2. Exhaustive photooxidation of phenol (“mineralization”). The circle symbolizes a micrometer large aggregate of semiconductor nanocrystals

Upon changing the Fe:Ti ratio, it turned out that films with a 1:1 ratio ($Fe_2Ti_2O_7$)[14] enable a visible light reduction of dinitrogen by ethanol. Initially formed ammonia is successively oxidized to nitrate (about 40 μmol) by traces of oxygen[15,16]. Since only reducing agents were active, which generate in the oxidative step a strongly reducing radical, we postulated a two-electron reduction of dinitrogen. By analogy with the *current amplification effect* in photoelectrochemistry we assume that the hydroxyalkyl radical (Scheme 3, steps 1, 2) injects an electron into the conduction band, resulting in the formation of two electrons, although only one quantum of light is absorbed. We proposed the term *redox amplification effect* for this property of reductants.[17] We note that only films which exhibit a current amplification in photoelectrochemical experiments are active in N_2 fixation. Thus, a proton-coupled two-electron/one photon reduction to 1,2 diazene becomes feasible (Scheme 3, step 3). Successive disproportionation, photoreduction, and a thermal catalytic oxidation step (Scheme 3, steps 4, 5) lead to the products. Since ethanol can be replaced by ubiquitous humic acid, and oxidative weathering of ilmenite minerals could form iron titanates, the question arises if a non-enzymatic nitrogen fixation may operate in nature. It is known that rutile containing desert sands upon UV irradiation generate a few micromoles of ammonia.[18]

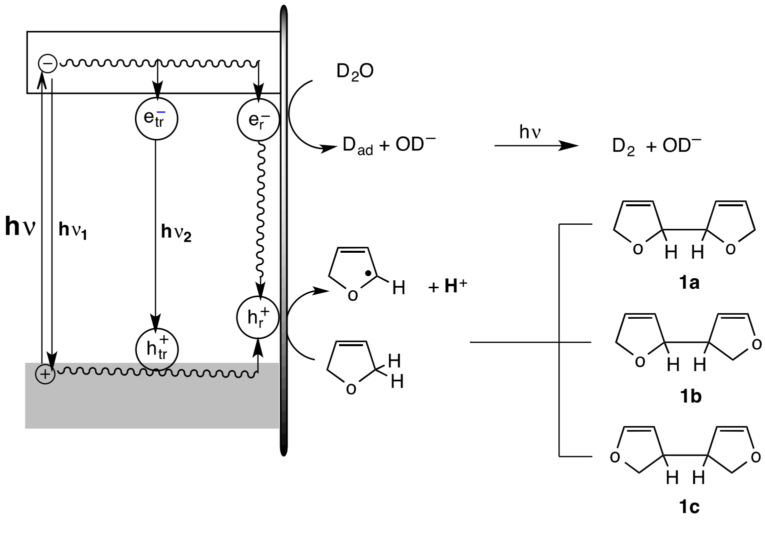


Scheme 3. Mechanistic scheme of nitrogen fixation at an iron titanate film

Dehydrodimerization of Olefins

The first example of the synthesis of a hitherto unknown compound by semiconductor photocatalysis is the anaerobic dehydrodimerization of cyclic allyl and enol ethers.[19,20]Zinc or cadmium sulfide can be used as photocatalysts. With the former catalyst, suspended in aqueous 2,5-dihydrofuran (2,5-DHF), irradiation by UV light produces in four days four liters of hydrogen and 10 g of the dehydrodimers **1a-d** (Scheme 4). [21] Detailed mechanistic investigations reveal that (i) quenching studies indicate that emitting and reacting electron-hole pairs are different, (ii) using D_2O leads to a decrease of the D_2 content from initially 90% to 40% after one hour of irradiation, whereas the sum of $HD+H_2$ increases from 10% to 60%. (iii) No product formation occurs in the absence of water, (iv) water is not consumed. The two last results can be explained by the nature of the two IFET reactions (Scheme 4). Accordingly, water is consumed in the reductive IFET to hydrogen and hydroxide ions. But the latter recombine to water with protons formed in the oxidative IFET. We note that in the many "sacrificial" hydrogen-forming systems the generation of D_2 is usually taken as a proof of water reduction. In view of our results, that is a *necessary* but not *sufficient* criterion. In many cases the reducing agent may deliver not only electrons but also protons and the reduction is only intermediary without consumption of water.

The allylic radicals formed in the oxidative IFET step reveal an unexpected high chemoselectivity. To 90% they undergo C-C coupling to the dehydrodimers whereas in homogeneous solution they may also disproportionate, add to double bonds, and undergo electron transfer. This significant difference becomes explicable since adsorption experiments evidence that 2,5-DHF adsorbs at each zinc surface center, providing an ideal spatial arrangement for C-C bond formation. Thus, the heterogeneous nature of the photocatalyst allows in addition to photoredox activation, also chemoselective radical bond formation.



Scheme 4. ZnS catalyzed photodehydrodimerization of 2,5-DHF

Semiconductor Photocatalysis Type B

As depicted in Schemes 1,2 the primary IFET products are radical ions. In the case of organic substrates their reactivity is well investigated, consisting predominantly of bond cleavage and electron transfer. Classical examples are fast deprotonation and dehalogenation reactions. Due to the more favorable driving forces IFET and deprotonation often occur in a concerted fashion (Eq. 3,4).

$$ArCH_3 + h_r^+ \rightarrow ArCH_3^{+\cdot} \rightarrow ArCH_2^{\cdot} + H^+ \qquad (3)$$

$$RCH_2X + e_r^- \rightarrow RCH_2X^{-\cdot} \rightarrow RCH_2^{\cdot} + Cl^- \qquad (4)$$

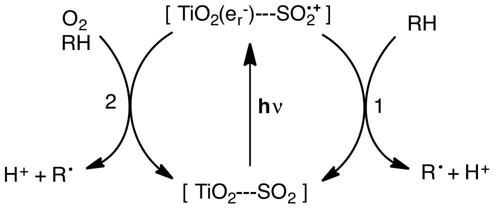
In almost all investigations the final products are formed in very small amounts and identified by analytical methods. Only very rarely, they were isolated on a preparative scale.[22]Furthermore, the products were well-known and usually obtained easier by non-photochemical pathways.[23] Contrary to that, we show in the following that semiconductor photocatalysis opens new preparative pathways to previously unknown addition products between unsaturated organic compounds. And, it enables Vis light activation of saturated alkanes, previously performed only with UV light.

Alkane Sulfoxidation

A further central topic of catalysis is alkane activation. A very rare example of a technically applied reaction is the photosulfoxidation of alkanes (Eq. 5). In a typical process forty medium pressure mercury lamps (l = 171 cm, diameter = 10.6 cm) dipping into a SO_2/O_2 saturated (C_{16}-C_{20}) mixture give rise to several tons of high-valued wax-like detergent pellets per day. Key steps of the

$$R\text{-}H + SO_2 + \tfrac{1}{2}\, O_2 + UV \rightarrow RSO_3H \qquad (5)$$

mechanism are absorption of UV light by SO_2, followed by hydrogen abstraction of its triplet state from the alkane. The generated alkyl radical adds to SO_2 and subsequent addition to O_2 produces the sulfonic acid under regeneration of a new starter alkyl radical, without the necessity of SO_2 light absorption. Therefore the over-all reaction is a photoinitiated radical chain reaction. However, in the technical process continuous UV irradiation is applied to compensate for radical



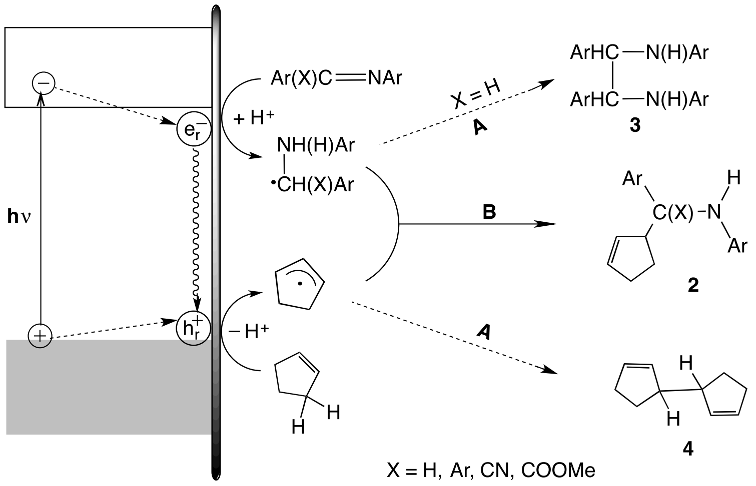
Scheme 5. Postulated titania catalyzed visible light photosulfoxidation. RH = n-hexane, cyclohexane, adamantane

loss through side reactions. When the photosulfoxidation is performed in the presence of titania powder, a visible light induced chain reaction becomes feasible allowing the use of simple tungsten lamps.[24]The reason for this surprising observation is that SO_2 forms with titania a yellow surface complex which becomes the light absorbing species.[25] The resulting optical electron transfer generates a reactive electron and a sulfur dioxide radical cation. Alkane activation may occur via proton-coupled oxidation (Scheme 5, step 1) and H-abstraction via intermediary OH and HO_2 radicals (Scheme 5, step 2). In laboratory experiments product yields were in the range of 40%. [26]

Linear Addition of Olefins to Imines and 1,2-Diazenes

When in the photodehydrodimerization experiment discussed above an organic electron acceptor is added, hydrogen evolution is completely inhibited and hitherto unknown addition products between the inhibitor and the unsaturated ether or olefin are formed. Especially active are 1,2-diazenes and imines as electron acceptors and cyclic olefins (having allylic hydrogen atoms) as donors. Isolated yields of the hitherto unknown products are in the range of 50-75%. Scheme 6 schematically summarizes the proposed mechanism. The primary radicals formed in the two proton-coupled IFET reactions predominantly undergo regioselective C-C bond formation affording the linear addition product **2**. A great variety of imines (Y-

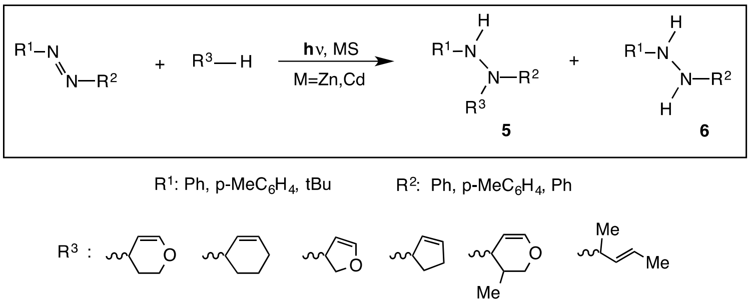
C(X)=NPh; X = H, Ar, CN, COOR; Y = Ar, 1-adamantyl) exemplifies the general applicability of this convenient synthetic procedure.[27] As by-products of the type B reaction also **3** and **4** are obtained through a type A process.



Scheme 6. CdS catalyzed addition of cyclopentene to an imine

Surprisingly, the radical C-C coupling to the hydrodimer **3** is diastereoselective in the case of N-adamantylimines and depends on the nature of the olefin, although it is not a reaction partner. Recalling that the radicals have to diffuse in a solvent-solute-surface layer where also the olefin is adsorbed, its steric influence becomes explicable. Thus, the olefin is a substrate for the type B reaction, but a stereodirecting spectator for the type A reaction.

In the case of 1,2-diazenes as acceptor substrates, allylhydrazines **5** and hydrazo compounds **6** are obtained as major and side products, respectively (Scheme 7). Key steps of the mechanism are analogous to Scheme 6. Surprisingly, the rate determining step is not C-N coupling but the preceding radical diffusion as indicated by the slightly positive activation volume.[28]



Scheme 7. Semiconductor catalyzed photoaddition of olefins and enolethers to 1,2-diazenes

Summary and Outlook

Simple inorganic semiconductors can act as heterogeneous photosensitizers for the redox activation of small molecules by visible light. Analogous to photosynthesis the photogenerated charges undergo concerted, proton-coupled reduction an oxidation reactions. The formed radicals can undergo chemo- and regioselective C-C and C-N coupling reactions in a solvent-solute surface layer. Thus, the photoexcited semiconductor enables not only sensitization by electron transfer, but due do its heterogeneous nature it controls also – different from homogenous systems – the conversion of primary into final products. Visible light activation of dinitrogen and alkanes, and novel addition reactions of olefins to imines and 1,2-diazenes demonstrate the power of semiconductor photocatalysis. The interdisciplinary nature of this field between chemistry, physics, and ecology may induce new developments in the areas of chemical utilization of solar energy and environmental science.

1 The efficiency of the conversion of light into reactive surface charges is presently in the range of 5-10%. This rather low value often prevents technical application. For improvement more basic research is necessary in this interdisciplinary field between photophysics and solid state chemistry.

2 For recent reviews see e.g. a) Kisch, H. Semiconductor Photocatalysis-Mechanistic and Synthetic Aspects. *Angew. Chem., Int. Ed.* **52**, 812-847, (2013); b) *Semiconductor Photocatalysis*, Wiley, New York, 2015.

3 Exciton binding energies are in the range of 23.0 - 0.0023 kcal/mol. The value of ZnS is 0.7 kcal/mol. Charge distances (Bohr radius) amount to a few nanometers.

4 In such thermodynamic estimations the band edge values are taken as approximate potentials of the reactive charges. IFET reactions are often proton-coupled, similar to photosynthesis.

5 In the case of *Indirect Semiconductor Photocatalysis* the substrates or substrate- surface complexes absorb the light.

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20 See ref. 1a.
21 0.2 g of ZnS were suspended in 150 mL of 2,5-DHF/H2O = 1:1 (v/v) and irradiated with a 150 W high pressure mercury lamp. Isolated yield of **1a-c** = 40%.
22 That means isolation of at least a few hundred milligrams of products.
23 See ref. 2b, Chapter 5.4.5.
24 Parrino, F., Ramakrishnan, A., Damm, C. & Kisch, H. Visible-Light-Induced Sulfoxidation of Alkanes in the Presence of Titania. *ChemPlusChem* **77**, 713-720, (2012).
25 Thus, the reaction can be classified as indirect semiconductor photocatalysis. See ref.5.
26 In a typical experiment 30 mg of TiO_2 were suspended in a solution of 0.136 g of adamantane in 15 mL of acetic acid and irradiated with a tungsten halogen lamp under a purge of $SO_2/O_2 = 1/1$ (v,v).
27 An example may demonstrate the simple procedure: To a suspension of anaerobically prepared 0.30 g of CdS in 200 mL

of MeOH are added 1.55 g of N-phenylbenzophenone imine and 36 g of α-pinene. After irradiation with a tungsten halogen lamp for 20 h, removal of CdS, and crystallization from n-heptane 1.64 g (72%) of the corresponding white homoallyl amine are obtained.

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Techniques for Characterizing Chain Propagation in Visible-Light Photoredox Catalysis

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The field of photoredox catalysis has garnered increasing attention from the synthetic organic community in recent years, as the visible-light promoted transformations offer many advantages such as mild reaction conditions, broad functional group tolerance, and increased temporal and spatial control.[1] Despite all the recent advancements in the field, many of the new discoveries take place in the absence of knowledge of the excited-state kinetics as well as an understanding of the underlying mechanisms. One method that is commonly used throughout the literature to probe the underlying mechanism of the transformation of interest is a light on/off experiment. In these experiments, it is stated that if a chain reaction is present, conversion should be observed during the period in which the light source is switched off. However, this is unfortunately not the case in the extended time-scales frequently used, as chain reactions normally terminate on the millisecond to second timescale. This issue may stem from the lack of quantitative methods that can be easily implemented in synthetic laboratories. In order to alleviate this issue, we have recently developed a chemical actinometer based on the ubiquitous photocatalyst, tris-(2,2'-bipyridyl)ruthenium(II) chloride ($Ru(bpy)_3Cl_2$), as well as an updated intermittent illumination technique using modern LED technologies.[2] These techniques should provide researchers with the mechanistic tools required to properly characterize chain propagation in the transformation of interest.

Our visible-light $Ru(bpy)_3Cl_2$ actinometer is based on the well-known singlet oxygen ($^1O_2$) mediated oxidation of 1,9-diphenylanthracene (DPA) to the corresponding endoperoxide (Figure 1). The consumption of DPA can be easily monitored by UV-Vis spectrophotometry, as DPA exhibits a distinct absorption band at

372 nm (ε = 11,000 $M^{-1}cm^{-1}$), which allows for facile quantification (Figure 1). Importantly, this band is not obscured by the metal-to-ligand charge transfer (MLCT) of Ru(bpy)$_3$Cl$_2$ (λ_{max} = 452 nm), allowing for facile quantification in the presence of the photosensitizer. Using the well-established ferrioxalate actinometer, we determined the quantum yield (Φ) of our Ru(bpy)$_3$Cl$_2$ actinometric system to be 0.019±0.001. This actinometer provides many advantages compared to other visible-light actinometers, such as the ferrioxalate actinometer.[3] For example, the Ru(bpy)$_3$Cl$_2$ actinometer is easy to work with, and can withstand longer irradiation times and higher light intensities that are typically employed in photoredox catalysis. Our Ru(bpy)$_3$Cl$_2$ actinometer does not require any developing agents, shows a linear relationship to power dependence, and it is also comprised of all commercially available reagents. Perhaps most importantly, there are no concerns relating to wavelength specificity, as the actinometer is also the photocatalyst. All that is required for spectral matching is to use the same concentration of Ru(bpy)$_3$Cl$_2$ in the actinometer as was used for the photoredox transformation of interest, which greatly simplifies the actinometry measurement.

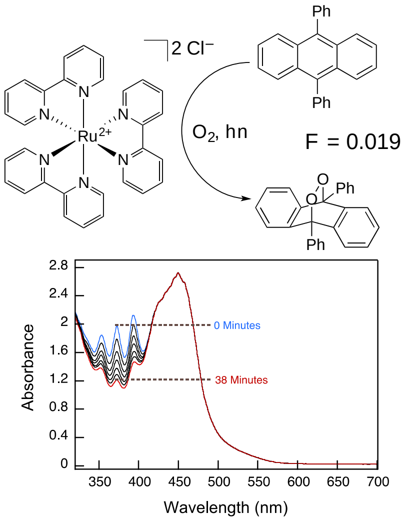

Figure 1. (Left) Scheme of the Ru(bpy)$_3$Cl$_2$ mediated visible-light actinometric system. (Right) Representative UV-Vis spectra from a typical actinometric experiment.

However, in many cases one cannot simply rely on actinometry alone to determine whether or not a propagating chain is involved in the underlying mechanism. Therefore, we have updated the "rotating sector" method for characterizing chain reactions using modern LED technologies.[4] This method is capable of allowing intermittent illumination from the microseconds to minutes timescales, including those relevant to typical chain propagation lifetimes, usually in the millisecond range. Coupling this method with the $Ru(bpy)_3Cl_2$ actinometer enables both the measurement of the **Φ** for a reaction, as well as the measurement of chain propagating lifetimes.

In our intermittent illumination set up, the LED is powered by a constant current driver and controlled by a digital delay/pulse generator. This allows for digital control over the pulse length, light intensity, and the light-to-dark ratio which makes the system quite versatile and user friendly.

This intermittent illumination method can be used for both qualitative and semi-quantitative characterization of chain reactions. Qualitatively, one can demonstrate the involvement of a chain reaction by demonstrating a non-linear dependence between conversion and the rate and mode of sample illumination (Figure 2), as one would expect that the rate of photon delivery should have no effect for a transformation free of chain reactions; that is, only the total energy absorbed is relevant, not the mode of energy delivery. On the other hand, this method also remains one of the easiest ways to experimentally determine the lifetime of a propagating chain (**τ_s**). This can be estimated by taking the point of 50% difference on a graph of conversion versus the log of the light on period (t_{on}). For the example shown in Figure 2, this corresponds to a **τ_s** of 19 ms for the $Ru(bpy)_3Cl_2$ mediated oxidation of benzhydrol using 4-cyano-*N*-methoxypyridinium as the chain amplifier.[5] This reaction was also found to have a **Φ** of 4.21, unequivocally confirming the presence of chain propagation in the overall reaction mechanism. We note that while in this particular case the value of **Φ** is sufficient to conclude that this is a chain reaction, there are many cases where the value of **Φ** can be well below one even if the reaction involves a chain process, as these values also reflect the yields of initiation that can be quite low.

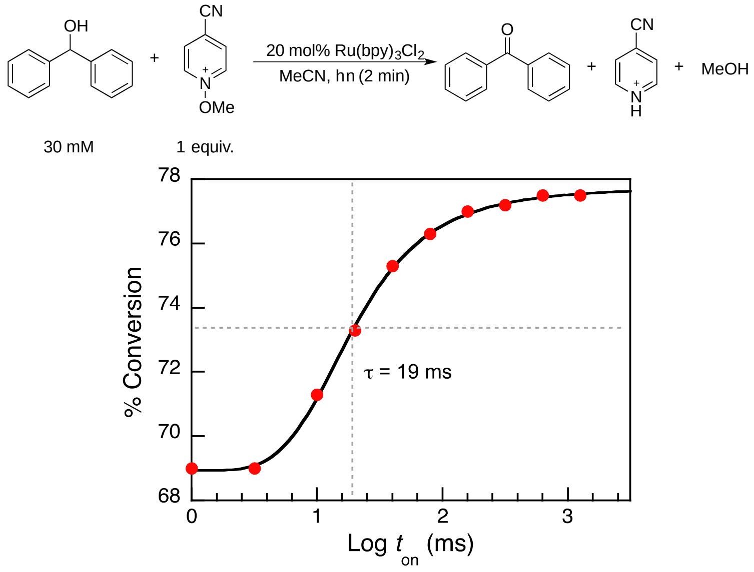

Figure 2. Intermittent illumination data for the $Ru(bpy)_3Cl_2$ mediated oxidation of benzhydrol to benzophenone.

Our $Ru(bpy)_3Cl_2$ based visible-light actinometer and updated intermittent illumination method should provide researchers with useful tools to characterize the involvement of chain reactions in photoredox transformations. The $Ru(bpy)_3Cl_2$ actinometer offers many advantages, which includes the fact that the actinometer is also the photocatalyst, eliminating the requirement for spectral matching. Our updated intermittent illumination method is comprised of modern LED technologies, and can be employed both qualitatively to demonstrate the involvement of chain reactions, as well as semi-quantitatively to determine the lifetime of chain propagation. We envision that these methods will have great implications in the field, as they provide researchers with methods that can be easily implemented without the need for specialized equipment not typically found in synthetic laboratories.

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Simulating solar-light conditions in UV driven heterogeneous photocatalysis

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Despite large number of papers some aspects of the solar driven heterogeneous photocatalytic reactions still need clarification. One of them is the proper experimental setup which would reflect real exterior conditions on the one hand, and, on the other, it could produce kinetic data under strictly defined laboratory conditions. Here we briefly report on heterogeneous photocatalytic oxidation with titanium dioxide carried out in a specially designed opto-chemical apparatus with direct implications to outdoor light conditions. For a long period, local (in geographic sense) UV solar light intensities were monitored and the recorded values used as inputs in experiments performed on preciously calibrated optical system, in which each position was associated with a specific intensity of the narrow UV-A photon flux. The model substrate, Acid Orange 7 (AO7) belongs to the class of azo dyes. Photocatalytic activities were evaluated as initial rates (pseudo-first order assumption) of AO7 oxidation (initial concentration $c_{Ao} = 10^{-4}$ mol L^{-1}) under UV-A illumination.

For a period of 12 months the UV light intensities of the solar photon flux were monitored at the level of the university flat roof (GPS Loc: 50°39'58.829"N, 14°1'54.659"E, Altitude: 195 m a.s.l.) regularly at 2 p.m. (CET), on days when sky was empirically assessed as “clear and bright”. These records are shown in Fig. 1. The increasing trends for the seasons when winter exchanges for spring, and spring for summer, are evident. It might be summarized that the recorded values were spanning overall from 0.3 (January) up to 6.5 mW/cm^2 (July), and from 0.6 in February up to 2.5 mW/cm^2 in the beginning of spring.

The reaction was first tested for the light intensity 3.7 mW/ cm^2 (and narrow wavelength 375 ± 5 nm) established as distinctive position on the specially designed optical bench involving a photoreactor (Fig. 2). This value corresponds to the day peaks of

UV solar light intensities in the middle of May (Central European geographic location).

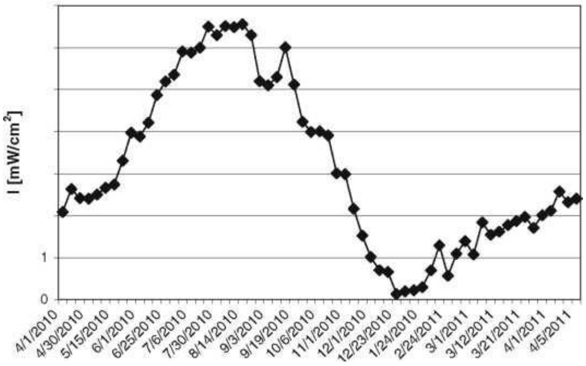

Figure 1. Outdoor UV light intensities (GPS Loc: 50°39'58.829"N, 14°1'54.659"E, Altitude: 195 m a.s.l.)

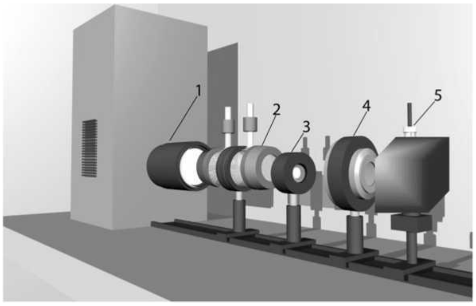

Figure 2. Experimental setup: *1* polychromatic lamp with cooling water cylinder, 2 water filter, *3* monochromatic filter, *4* mechanical shutter, *5* quartz, magnetically stirred and heated cell (with a jacket for isothermal performance)

The used catalyst was the low surface area AV01 (~ 10 m^2 g^{-1}, Precheza). Its evaluated band gap corresponded well to the chosen monochromatic filter (375 nm). It`s very good performance confirmed the fact that for the heterogeneous photocatalytic process large surface area is not necessarily needed. Next, the reaction tests were performed at constant temperature 40 °C, but varying the UV light intensity over a wide interval from 0.3 to 5 mW/cm^2. The conversion of AO7 was plotted as function of this parameter. Up to 1 mW/cm^2, the achieved conversions had been increasing steeply. In the next part, up to 2 mW/cm^2, the conversion improvement was much lower, but still evident. Above the 2.5 mW/cm^2 level, the increment was already negligible. It could be concluded that the reaction follows zero order kinetics with respect to the involved photons above this level, as generally accepted. On the other hand, below this level, the process does not proceed in the kinetic regime, the reaction order of photons as reacting particles is not precisely zero. Finally, the oxidation of AO7 was performed with AV01 at 6 different temperatures (12, 25, 35, 40, 50, 60 °C) and at 3.7 mW/cm^2. The evaluated kinetic data were expressed in the form of Arrhenius type plot (log l< j as function of 1/T). A linear dependency indicated that the first reaction step of transformation of AO7 proceeded with no contribution of diffusion and other non-ideal behavior. Details on the discussed topics could be found elsewhere [1-3].

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Photoredox Catalytic Applications in Organic Synthesis using Visible Light as Energy Source

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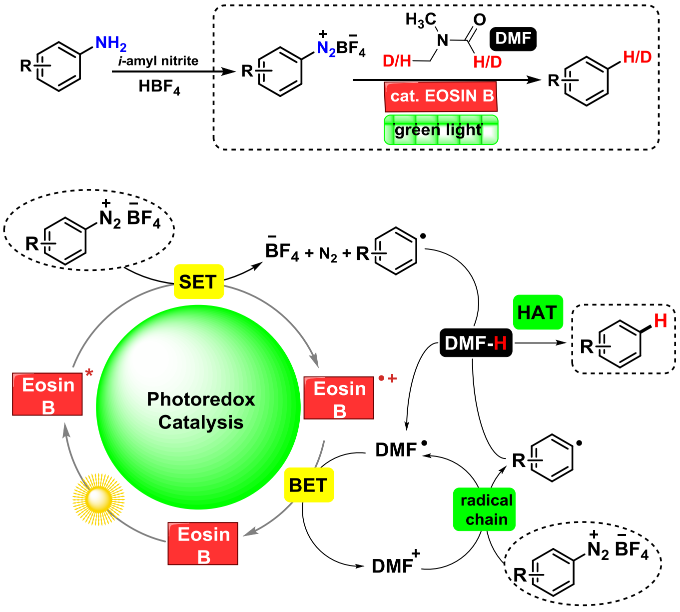
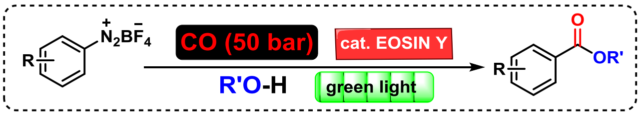
Visible light is a clean, inexpensive, and 'infinite' source of energy which has attracted considerable interest from the chemistry community only recently.[1] The Italian chemist Ciamician had already recognized a century ago that sunlight could be utilized as a promoter of organic reactions.[2] However, one fundamental impediment that significantly limits the development of photochemical processes is the inability of most common organic molecules to absorb light in the visible range. For that purpose, many investigations have been devoted to develop photoredox catalysts that are able to absorb visible light and mediate the desired chemical transformations by means of rapid electron-transfer processes. In the last few years, the application of organometallic (and a few organic) dyes to several chemical processes has emerged as a powerful synthetic technology enabling several organic transformations that are either impossible or impractical with conventional protocols.[3] This approach largely relies on the ability of metal complexes and organic dyes to engage in single electron transfer (SET) processes with organic substrates (mainly highly reactive substrates such as C–I, C(sp3)–Br and π bonds) upon photo-excitation with visible light.[4] Many of the common visible light photocatalysts are oligopyridyl complexes of ruthenium and iridium, typified by tris(2,2'-bipyridine) ruthenium(II), $Ru(bpy)_3^{2+}$. Moreover, their long-lived triplet excited states (e.g. 1100 ns for $Ru(bpy)_3^{2+}$) have been found to be stronger oxidants and/or reductants than the ground state. Thus, bimolecular electron transfer occurs in competition with deactivation pathways.

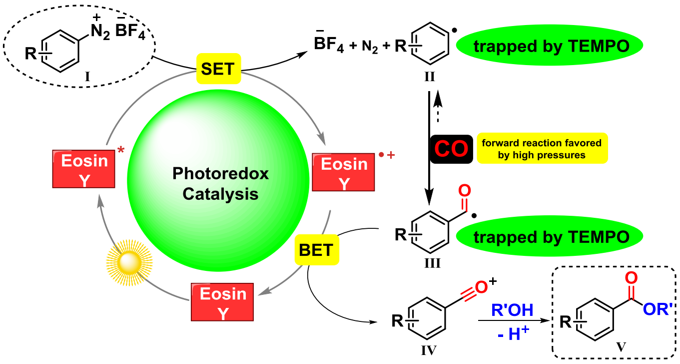
The coupling of such photon excitation by household light bulbs with organic redox processes has been applied to various bond forming reactions.[3f,5] Organic dyes such as methylene blue, rose Bengal, eosin, triphenylpyrylium salts or 9-mesityl-10-methylacridinium ion can also act as visible light photocatalyst giving rise to excited states capable of SET.[3c,6] There are very few synthetic applications of metal-free photocatalysts, so that new protocols with cheap organic dyes certainly make a strong impact on the art of sustainable synthesis. In this letter, I wish to highlight some of the investigations performed in my current research group led by Prof. Axel Jacobi von Wangelin, providing new metal-free organic synthesis applications in this vibrant Sunlight Photocatalysis field. In this context, a new visible light driven methodology has been recently developed which permits selective hydro- and deuterodediazonations of arenediazonium salts as a key step of deamination strategies (Scheme 1).[7] It is worth mentioning the absence of metals (eosin B as photocatalyst) or stoichiometric reducing agents in the protocol employed by comparison with conventional processes. On the basis of actinometry and DFT calculations, photoredox and radical chain pathways together with H-abstraction competition between the methyl and formyl group of the DMF have been found to be involved in the proposed reaction mechanism.



Scheme 1. Illustration of the proposed reaction mechanism for the hydrodediazonation by visible light.

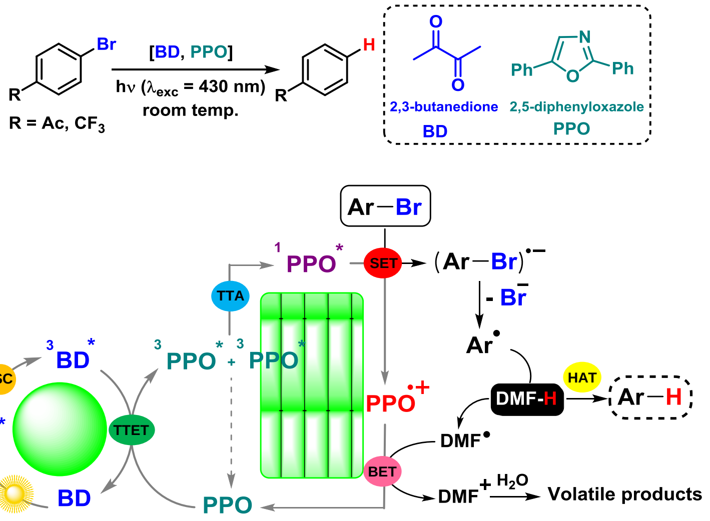
On the other hand, selective formation of C-C bonds is at the heart of organic synthesis and holds the key to the generation of structural complexity and diversity of fine chemical, bioactive, natural, and polymeric molecules. The past years have also witnessed the re-discovery of visible light as ubiquitous source of energy for C-C bond-forming reactions. Within this respect, our research group has dedicated efforts in using other C-based reagents such as carbon monoxide, CO. This C1 building block is the primary product of all chemical raw materials (coal, oil, gas, biomass) and finds extensive use in the industrial manufacture of fine chemicals, agrochemicals, materials, and pharmaceuticals.[8] Among the carbonylation products, benzoates are especially important structural motifs; their conventional synthesis largely use super-stoichiometric amounts of expensive and often hazardous organometallic species, expensive or toxic metal catalysts (Pd, Ni), and complex ligands (phosphanes, carbenes).[9] Thus, an alternative metal-free and base-free protocol for alkoxycarbonylations has been published that involves a one-electron redox mechanism that is driven by visible light in the presence of an organic dye as photocatalyst.[10] Arene diazonium salts as starting electrophilic agents, CO and alcohols constitute the ingredients for preparing alkyl benzoates in very good yields at room temperature using green LEDs (525 nm) as energy source in the presence of catalytic amounts of Eosin Y as cheap photosensitizer. The operating mechanism is shown in Scheme 2. After SET from the excited Eosin Y to the diazonium salt (I) and loss of N_2, an aryl radical intermediate (II) is formed. This species then are trapped by CO leading to an acyl radical intermediate (III) that is oxidized by back electron transfer giving rise to the highly electrophilic acylium ion (IV). This IV intermediate reacts efficiently with the corresponding alcohol to afford the benzoate ester (V). DFT calculations and radical trapping experiments have supported this novel catalytic photoredox process.





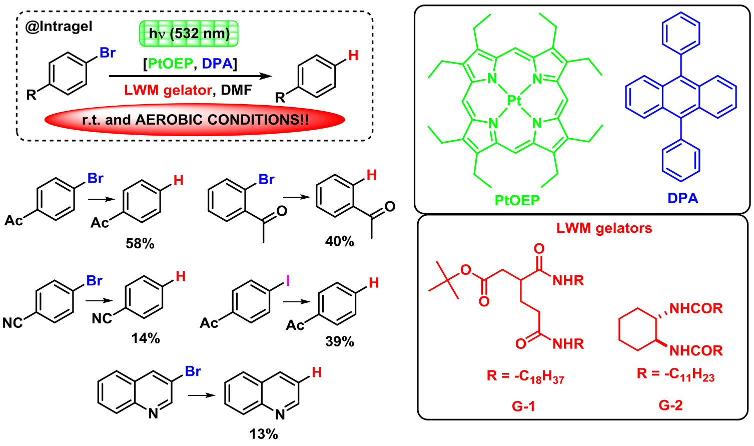
Scheme 2. Illustration of the proposed reaction mechanism for the metal-free carbonylation by photoredox catalysis.

Most of arene diazonium salts are not commercially available and not stable in the presence of air, being their employment sometimes prejudiced. Furthermore, the use of broad-spectrum lamps in photocatalytic reactions with arene diazonium salts is strongly discouraged as heterolytic C–N bond cleavage is achieved toward highly reactive aryl cation species.[11] Therefore, it would be of great interest to find novel methodologies using aryl halides which are the most elegant class of electrophilic reagents. However, bond-dissociation energy (BDE) of aryl–Br bonds (e.g., BDE_{PhBr} = 3.6 eV) considerably exceeds the maximum photonic energy of visible light (3.1 eV). Reduction potentials of non-activated aryl bromides (e.g., PhBr: –2.68 eV vs. SCE) are also beyond the excited triplet energies of common photoactive one-electron reductants (eosin Y: 1.9 eV; $[Ru(bpy)_3]^{2+}$: 2.0 eV; $[Ir(ppy)_3]^{+}$: 2.5 eV); even more so when considering the energy loss during ISC and structural reorganizations. As a matter of fact, activation of higher energy aryl halides (Br, Cl) using visible light is a significantly more challenging task. To overcome this limitation, we have reported for the first time that photon upconversion (UC) based on triplet-triplet annihilation (TTA) is a suitable technology for the activation of aryl bromides using visible light as energy source.[12] TTA-UC implies the association of multistep photochemical events (ISC = intersystem crossing; TTET = triplet-triplet energy transfer; triplet-triplet annihilation = TTA) to generate finally a high-energy delayed upconverted fluorescence. Therefore, a new combination of UC-TTA plus an SET-initiated reductive activation of aryl bromides has been demonstrated as a proof of concept (Scheme 3). Interestingly, the UC-TTA photophysical process has been assessed by metal-free dyes such as 2,3-butanedione (BD) and 2,5-diphenyloxazole (PPO) playing the role of sensitizer and annihilator, respectively. Once the formation of the delayed fluorescence of PPO as high-energy intermediate is obtained, this species are capable to reduce aryl bromides by SET, initiating the chemical steps. Fast cleavage of the radical anion of the aryl bromide leads to an aryl radical and rapid H-abstraction from DMF affords the formal reduced product. It is important to note that an exergonic back electron transfer process is occurring from the radical DMF to the radical cation of PPO, restoring PPO and giving cation DMF which hydrolyzes upon work-up to volatile products.



Scheme 3. Top: light-induced reduction of aryl bromides under TTA conditions. Bottom: proposed reaction mechanism involving TTA, SET and HAT as key steps (ISC=Intersystem crossing; TTET=Triplet-triplet energy transfer; TTA=Triplet-triplet annihilation; SET=Single electron transfer; HAT=Hydrogen abstraction transfer; BET=Back electron transfer).

Ongoing with this novel and promising methodology that involves both TTA-UC and SET-initiated processes, we wished to go one step further and develop this version to the adaptable nature of supramolecular fibrillar gel networks, which allows efficient and cooperative incorporation of donor/acceptor pairs while preserving the structural integrity of the bulk material. In collaboration with Prof. David Diaz Diaz at the Regensburg University, we have recently discovered the first intragel photoreduction of aryl halides using TTA-UC technique.[13] Surprisingly, the gel network provides a suitable stabilizing microenvironment to assess the challenging multistep process (*vide supra*) under aerobic conditions, room temperature and without additional additives such as bases or acids. Intragel photoreduction of several aryl halides in air are shown in Scheme 4 where platinum(II) octaethyl-porphyrin (PtOEP) as sensitizer and 9,10-diphenylanthracene (DPA) as emitter are embedded in two different supramolecular gel networks (N,N'-bis(octadecyl)-L-boc-glutamic diamide (G-1) and N,N'-((1S,2S)-cyclohexane-1,2-diyl)didodecanamide (G-2)) for comparison. These results demonstrates that low weight molecular (LWM) gelators can be used as confined reaction media or micro/nanoreactors, providing the background for more demanding photophysical processes such as TTA-UC.



Scheme 4. Intragel photoreduction of aryl halides in air.

Overall, successful applications in organic synthesis driven by visible-light photoredox catalysis have been well-established. In particular, TTA-UC technology holds great potential for challenging bond activations while retaining the benefit of mild reactions conditions by the use of lower-energy visible light. Finally, we have demonstrated the viability of soft gel materials as nanoreactors for photoreduction of aryl halides by means of TTA-UC methodology.

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Proton Transfer is Important in Water Oxidation on Hematite

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Solar water splitting is one of the most promising solutions for energy crisis in the near future.[1] Since Fujishima and Honda developed the great new concept of photoelectrochemical (PEC) water splitting on semiconductor TiO_2 in 1972,[2] there has been a tremendous expansion of researches on solar photocatalysis with semiconductor materials, especially TiO_2. Unfortunately, with the large band gap, TiO_2 can only be excited by ultraviolet irradiation which is above 3.2 eV. In the recent years, great efforts have been made to look for semiconductors with smaller bandgaps and appropriate energy levels. α-Fe_2O_3 (hematite) is a promising material with a desirable band gap of ~2 eV, which can theoretically convert 16.8% of the solar energy into hydrogen. [1]

Of the two half reactions of water splitting, water oxidation has

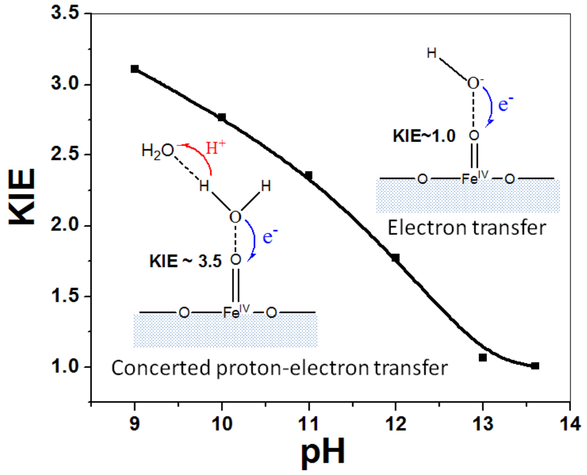

Figure 1. A schematic showing the different pathway of proton transfer under different pH conditions on hematite surface.

been considered to be the major bottleneck, relative to water reduction, due to the complicated coupled $4e^-/4H^+$ processes.[3] Previous studies on solar photocatalysis mostly focus on kinetics of electron transfer; but the significance of the kinetics of the proton transfer remains unexplored. Proton-coupled electron transfer (PCET) should play a pivotal role in water oxidation reaction because of its thermodynamic advantage by avoiding the high-energy intermediates.[4,5]

In a recent study, published in the *Journal of the American Chemical Society,* our group have used H/D kinetic isotope effect (KIE) experiments to obtain the direct information about proton transfer behaviour in the PEC water oxidation on hematite surface. In combination with electrochemical impedance spectroscopy (EIS), we successfully demonstrate that the surface hole transfer to a water molecule occurs via a concerted proton-electron transfer (CPET) pathway under near neutral conditions, where another water molecule act as the proton acceptor (Fig. 1). To the best of our knowledge, this work represents the first direct experimental evidence for a CEPT pathway for the water oxidation reaction on hematite surface. We further modulate the proton transfer process by using buffer bases to act as the much stronger proton acceptors, compared with water molecule, and much improved water oxidation activity can be obtained on hematite surface at near-neutral pH levels.[3]

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Decatungstate salts: convenient photocatalysts for solar light driven synthesis.

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Solar light is the environmental-friendly energy source par excellence to convert light into chemical energy. Starting from the pioneering work of Giacomo Ciamician,[1-3] several efforts have been devoted to exploit such a benign light source. The main problem is that the majority of organic compounds are colorless, making troublesome solar light induced transformations. The recent developments in the use of visible (solar) light absorbing photocatalysts, however, gave an impressive advancement in the field.[4]

We were recently involved in the use of TBADT (tetrabutylammonium decatungstate, $(n\text{Bu}_4\text{N})_4[\text{W}_{10}\text{O}_{32}]$), a photocatalyst that is able to cleave homolytically X-H (mainly C-H) bonds in organic substrates upon solar light absorption.[5] The mechanism of action is depicted in Figure 1 (left). The hydrogen atom abstraction step causes the formation of nucleophilic radicals prone to add to electron-deficient olefins. Back hydrogen donation from the reduced photocatalyst (TBADT-H$^\bullet$) finally leads to the hydroalkylated alkene and allows the regeneration of the photocatalyst. The synthesis is 100% atom economy. The reaction can be carried out by pouring the solution in a glass vessel under sunlight (Figure 1, right).[6] Upon irradiation the solution turns blue (the color typical of the TBADT-H$^\bullet$ form), indicating that the photocatalytic process is occurring. Our approach has several advantages from the environmental point of view, since no artificial energy must be supplied for the process.[6]

Different hydrogen donors (R-H) can be adopted in the conjugate addition onto dimethyl maleate (a typical Michael acceptor), as exemplified in Scheme 1. Thus, the C-H bonds in cyclohexane, DMF and 1,4-dioxane were chemoselectively cleaved and compounds **2-4** were obtained in a good yield upon bulb to bulb distillation of the end mixtures.[6]

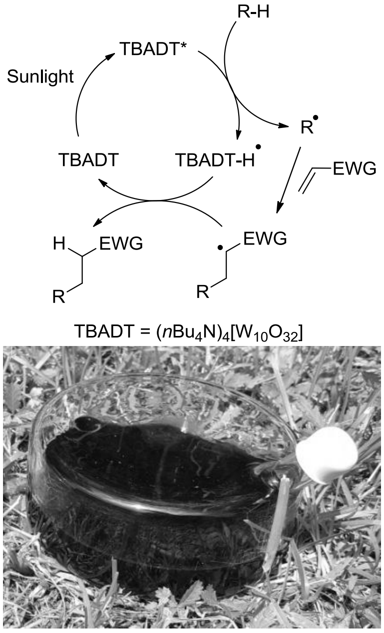
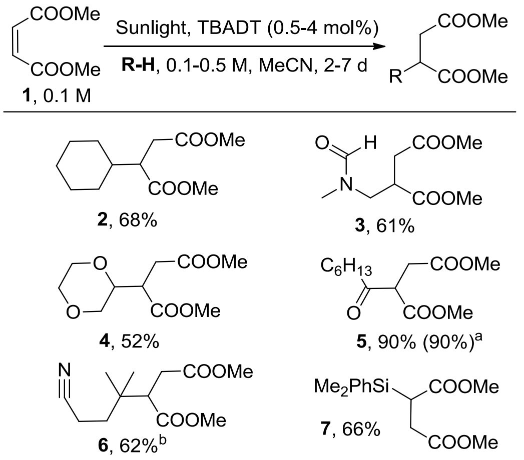


Figure 1. A schematic view of the mechanism of action of TBADT photocatalyzed hydrogen atom abstraction (HAT) reactions in the functionalization of electron-poor olefins (left). Reaction mixture exposed to sunlight (right; picture by Luca Capaldo - PhotoGreen Lab, University of Pavia).

Acyl radicals can be likewise smoothly formed by C-H cleavage of the C(=O)-H bond. Acylation of **1** with heptaldehyde afforded ketone **5** in ca. 90% yield. Interestingly, we were able to increase the concentration of the reagents up to 0.5 M maintaining the same yield. The reaction was carried out on 100 mL solution and ca. 10 g of **5** were obtained after 9 days irradiation.[6] The selective C-H activation in acyclic nitriles (e.g. isocapronitrile) is another example where the selective γ-methine hydrogen atom abstraction led to cyanoester **6**.[7] Cyclopentanones likewise functioned as hydrogen donors and were selectively β-alkylated in the presence of electron-poor olefins, such as acrylonitrile.[8] The photocatalytic activation of a Si-H bond was exploited in the direct hydrosilylation of alkenes, as shown in Scheme 1 for compound **7**.[9]



[a] **1** (0.45 M), heptaldehyde (0.5 M); ca. 10 g of compound **5** isolated after 9 days irradiation. [b] 0.5 M **1** was used in the presence of 20 equiv. isocapronitrile

Scheme 1. Photocatalyzed functionalization of dimethyl maleate **1**.

In conclusion, the use of TBADT allowed for the development of a series of selective, efficient and atom economic reactions under mild and energy saving conditions. Notably, no stirring, no heating/cooling are required during the process and (natural) sunlight is the only energy employed.

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PILLS OF HISTORY

At the origin of photochemistry. From the phototropy to the first attempts to rationalize a photochemical reaction in the experience of Maurizio L. Padoa.

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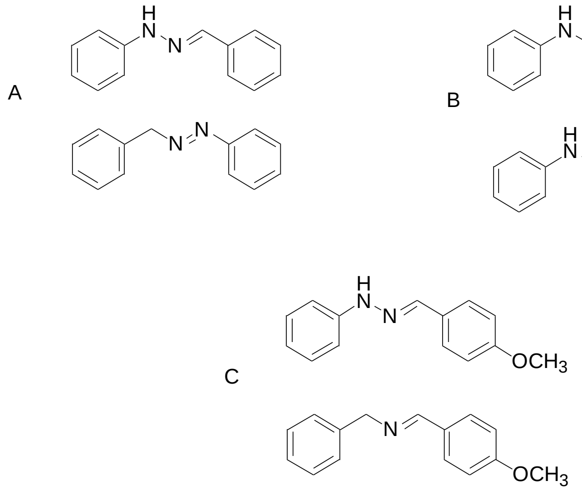
Maurizio Leone Padoa was an assistant of Giacomo Ciamician. Usually, most of the photochemical work on photochemistry was performed by Ciamician with the help of Paul Silber, and we know all on this work. On the other hand, the photochemical work of Maurizio Padoa is completely forgot. He worked with Ciamician until 1920 when he was designated as extra professor at the University of Cagliari, and then he was nominated full professor at the University of Parma. In 1924 he returned in Bologna to maintain the chair of Industrial Chemistry. He continued to study the photochemical properties of some organic and inorganic compounds. During Fascism he had some problems. First, he firmed the appeal of antifascist intellectuals promoted by Benedetto Croce. Then, he was suspended because his suspect on an assistant, a fascist assistant, and transferred to the University of Modena. In 1938, with the promulgation of race laws in Italy, being Padoa of Jewish religion, he was expelled from the University. In 1944 he was taken by fascist and nazist soldiers in his farm. He dead at Auschwitz.

He started his work in photochemistry studying the phototropy of some compounds. The hypotheses were those described by Stobbe that reported that a photropic transformation does not modify the chemical compounds (now we know this is not true), and that if A is the colored form of the phototropic compound and B is the uncolored form, we have the formation of a solid solution. Padoa decided to study the phototropic behavior of the phenylhydrazone of benzaldehyde in the presence of compounds with similar structure able to give a solid solution with the phototropic compound.[1] He studied the phototropic behavior of the pairs of compounds reported in the Scheme 1.



Scheme 1.

The phenylhydrazone of the benzaldehyde is a phototropic compound, but it needs a long time to return to the original color. In the presence of 4.6% of the second compound in the pair A discoloration occurred rapidly; on the contrary, when 4.92% of the second compound in the pair B is present, the phenylhydrazone of the benzaldehyde cannot react. Finally, the presence of the second compound in the pair C induced a rapid coloration of the mixture.

In another article Padoa studied the phototropic propertie of some arylhydrazones showing that hydrazones obtained from α–naphthylhydrazine did not show phototropy while those obtained from β-naphthylhydrazine were phototropic compounds. Furthermore, most of the compounds obtained from 4-methylphenylhydrazine showed phototropic properties (Table 1).[2]

Table 1.

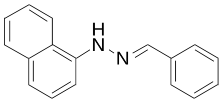
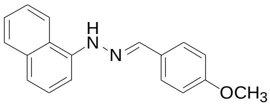
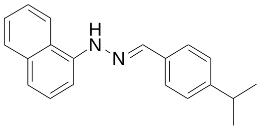
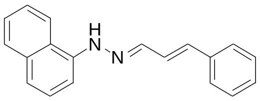
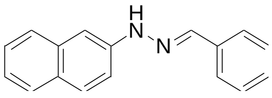
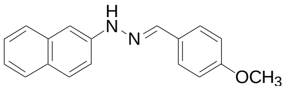
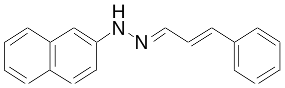
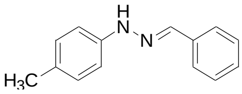
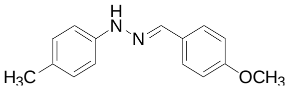
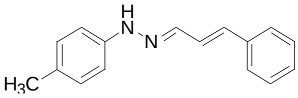
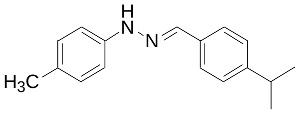
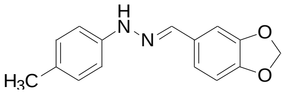
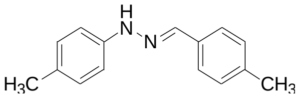
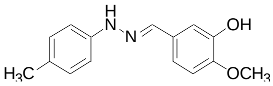
Compound	**Phototropy**	**Color**	**Retrocession time**
	no		
	no		
	no		
	no		
	yes	pink	4-5 days
	yes	pink	Few days
	yes	chocolate	30 h

Table 1. *Continued*

Compound	**Phototropy**	**Color**	**Retrocession time**
	yes	red	Few days
	no		
	yes	chocolate	7-8 h
	yes	red	10 h
	yes	red	12 h
	no		
	no		

Furthermore, he showed that, when 3-methylphenylhydrazine was used to form the corresponding hydrazones the obtained compounds were phototropic, while, 2-methylphenylhydrazine gave hydrazones that were not phototropic (Table 2).[3]

Table 2

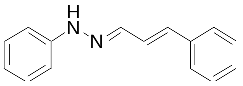
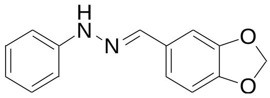
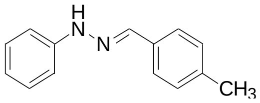
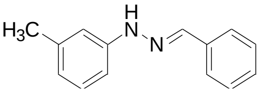
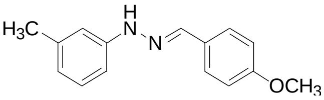
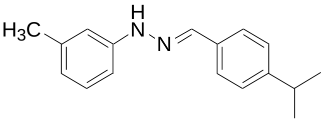
Compound	Phototropy	Color	Retrocession time
	yes	chocolate	Few days
	no		
	no		
	yes	pink	-
	no		
	yes	pink	-

Table 2. *Continued*

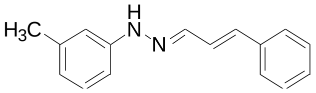
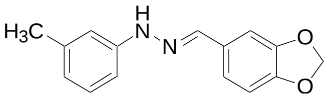
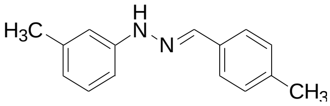
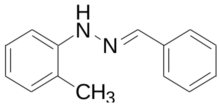
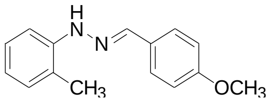
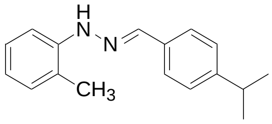
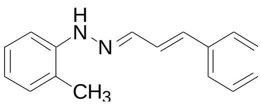
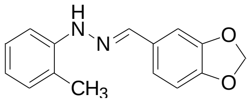
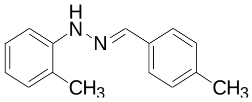
Compound	Phototropy	Color	Retrocession time
	yes	chocolate	-
	yes	pink	3-4 days
	no		
	no		
	no		
	no		
	no		

Table 2. *Continued*

Compound	**Phototropy**	**Color**	**Retrocession time**
	no		
	no		

Continuing this study on the correlations between structure and phototropy, he confirmed that β-naphthyl hydrazones are phototropic, while hydrazones obtained from 3,4-dimethylphenylhydrazine were not phototropic.[4,5] Also the hydrazones synthesized from 3,5-dimethylphenylydrazine did not show phototropy.[5] On the contrary, hydrazones prepared from 2,4-dimethylphenylhydrazine were phototropic.[4]

When the hydrazones were synthesized starting from 4-bromophenylhydrazine, some of them showed a phototropic behavior.[6] On eight hydrazone prepared from 4-methoxyphenylhydrazine five were phototropic.[7]

Several osazones showed a phototropic behavior (Table 3). In this case the presence of a substituent in *ortho* and *meta* position on the hydrazinic part of the molecule did not inhibit the phototropy. Osazones derived from α-naphthylhydrazine also showed phototropy. On the contrary, when 1-methyl-1-phenyl- or 1,1-diphenylhydrazine was used no phototropy was found in the corresponding osazones.[8-12]

After this comprehensive work on the nature of phototropic substances, Padoa started to study the presence of physical effect influencing the phenomenon.

Table 3

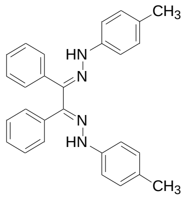
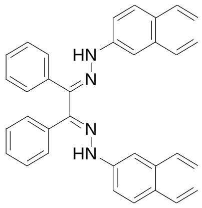
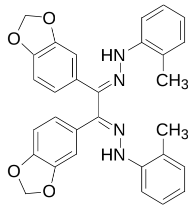
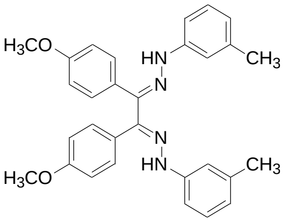
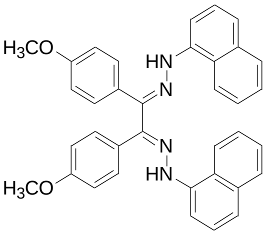
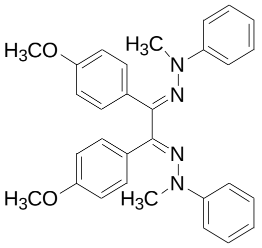
Compound	**Phototropy**
	yes
	yes
	yes
	yes

Table 3. *Continued*

Compound	Phototropy
	yes
	no

In a first paper he studied the change of photoelectric properties in a phototropic process.[13] However, at high temperature he observed changes of photoelectric properties during UV exposition in the absence of color modifications. Then, he concluded that phototropy and photoelectric effect were independent. At the same time, he studied the effect of the temperature on a phototropic change.[14] In the reaction of *o*-tosylhydrazone of piperonal the temperature coefficient (k_T) was 2.0 in the discoloration process and 1.06 in the coloration process. In the coloration process the temperature coefficient was lower in agreement with the low dependence from the temperature of a photochemical reaction. After this work, he studied the temperature coefficient of the phototropic modifications in salicyden–β–naphthylamine;[15,16] this compound had to phototropic forms, one of them was red, the other one was yellow. The formation of the red form (obtained through irradiation) had a $k_T = 1.47$ in agreement with a monomolecular process, while the formation of the yellow form (obtained in the dark) had a $k_T = 2.0$ in agreement with a bimolecular process. This behavior was in agreement with a process involving the following process.

$$A_2 \underset{\text{dark}}{\overset{\text{light}}{\rightleftharpoons}} 2A$$

Studying the photochemical behavior of the same substance by using monochromatic light, Padoa found that, with violet light, he found $k_T = 1.39$, with blue light 1.45, and with green light a value of 1.80, in agreement with the hypothesis that for photochemical processes activated with light at longer wavelength the temperature coefficient was higher.[17,18] Furthermore, the energy associated with a phototropic transformation was very low: by using the Mahler bomb, the difference between the heat of combustion of the red and yellow form of salicyden-β-naphthylamine was only 2.9 cal, a difference imputable to errors.[19] In another article Padoa described a new correlation he found.[20] In fact, he observed that the ratio between the temperature coefficients of the phototropic processes (coloration and discoloration processes) was the same of light intensity ratio need to maintain the same coloration for reactions occurred at two temperatures differing for 10 °C. In the case salicyden-β-naphthylamine, he found $k_T/k_{T-1} = 1.42$ and $I/I_{-1} = 1.405$.

The increase of the temperature coefficients with the wavelength was verified also in the case of the reaction of ammonium oxalate with $HgCl_2$ in the presence of tetrabromofluorescein.[21] In this case, with ultraviolet light a temperature coefficient $k_T = 1.05$ was observed, with blue light 1.21, with green light 1.75. The same behavior was observed in the photochemical reaction of chlorine with hydrogen.[22] The presence of the temperature coefficient in the photochemical reactions was observed also on photographic papers.[23]

Studying the reaction of chlorine with hydrogen in the presence of trace of iodine he found that, by using violet and blue light, the temperature coefficient increased in the range 0-20 °C but decreased in the range 20-40 °C.[24] The rate of the reaction showed a maximum. Padoa discussed this result on the basis of some hypotheses. Nernst formulated the hypothesis that the reaction occurred though the cleavage of Cl-Cl bong. However, Stern and Volmer did not admit the cleavage of this bond because the energy adsorbed to do not allow this cleavage. They preferred a hypothesis where the absorbed quanta (on the basis of known Einstein law) allowed the formation of different status, chemically active. Padoa considered the Nernst hypothesis more convincing and explained the negative temperature coefficient supposing that the molecular energy did not exceed a given value in order to react. Furthermore, he found that the temperature coefficient in this reaction reached a maximum by using white light: the ratio between k_T obtained by using white light and those obtained with blue and violet light was 1.62.[25] He supposed a different activation mechanism in function of the used light. These results have been confirmed in the photochemical bromination of cinnamic acid.[26]

In the photochemical oxidation of HI he found that the reaction occurred by using different lights. The efficiencies obtained with blue and green lights compared with that obtained using white light showed a neat increase by using green light.[27] In the complex the used of different lights increase the efficiency of the reaction. The same result was obtained for the reactions of $FeCl_3$ and $HgCl_2$ with oxalic acid. The results were interpreted considering that the reactions could occur with a different mechanism in function of used wavelength, on the basis of the hypothesis that different wavelengths would be absorbed by different parts of the molecules. In the oxidation of HI Padoa found that, in this case, the temperature coefficients decreased with the increase of the wavelength.[28] This behavior was explained assuming the different capability of the molecules to absorb light and react at the different wavelengths.[29] In the reaction of FeI_2 with iodine, considering the energy connected with the used wavelengths, assuming that 30 cal were sufficient to relax the I-I bond the ratio between the energy of light and 30 cal gave the results in agreement with the experimental results.[30] These results were confirmed by some other studies in this field.[31,32]

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ABSTRACT OF THESIS ON PHOTOCHEMISTRY

Laser Spectroscopy and Fluorescence Microscopy Applied to the Study of Nanosystems

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Ph.D. Thesis

One of the strategic lines of research worldwide, commonly known as Nanoscience and Nanotechnology, is focused on the development of new synthesis methods as well as developing analytic tools to manipulate the matter at atomic and molecular scales. The fast widespread and application of nanoscience (nanotechnology) in modern life is being possible thanks to the advances in the characterization of the synthetized materials. From the vast arsenal of characterization methods, laser spectroscopy and fluorescence microscopy techniques are ones of the most powerful tools, offering the possibility to unravel the physicochemical properties at different levels of complexity with a great ease of adaptation to the studied materials.

The main goal of this Ph.D thesis was to explore the relationship between the photochemical and photophysical properties exhibited by the studied materials (of relevance in Nanomedicince, Nanocatalysis and Nanophotonics) and their structures, as well as the effect of their immediate environment. To that end, the experimental work combined the use of steady-state observation, time-resolved (femto to millisecond regime) and space resolved (fluorescence microscopy, down the 250 nm) from ensemble average to single molecule level.

- ***Studies relevant to drugs encapsulation: Nanomedicine***

More specifically, the studies in this field were focused on understanding the photochemical/photophysical behaviours of the host-guest interactions. The ultrafast dynamics of selected molecular probes (8-hydroxypyrene-1,3,6-trisulfonate (*HPTS*) and *Coumarin 30* (*C30*)) as well as biologically relevant molecules (Lumichrome (*Lc*)) were studied in the presence of chemical (cyclodextrins) and biological (human serum albumin protein) hosts. The use of femtosecond to picosecond time-resolved techniques revealed how specific and nonspecific interactions influence the excited-state relaxation pathways of the encapsulated guests. Using selected dyes with specific properties, such as the capability to undergo charge (*C30 and Lc*) or proton transfer processes (*HPTS and Lc*), provided key information on how the local environment affects the rate constants of the involved processes and how they dissipate the energy excess to the host through specific and non-specific pathways (see for example (Figure 1).

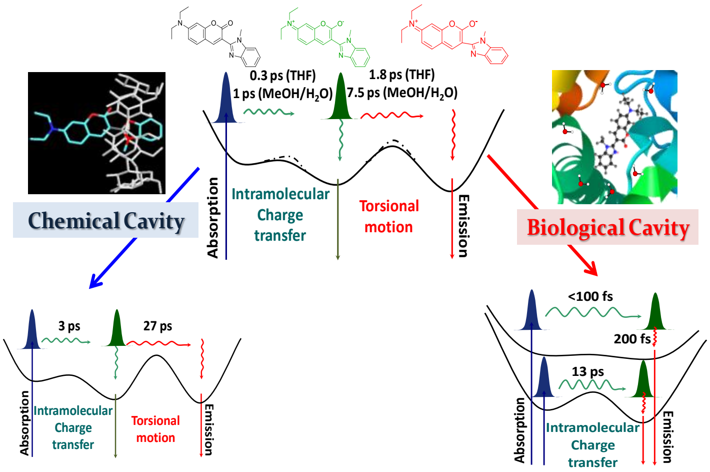

Figure 1. Schematic representation of C30 photobehavior (at S1) in solution, inside chemical (cyclodextrin) and in biological (HSA) cavities. These results were published in: C. Martin, B. Cohen, I. Gaamoussi, M. Ijjaali, and A. Douhal, "Ultrafast Dynamics of C30 in Solution and within CDs and HSA Protein" *J. Phys. Chem. B* **2014**, *118*, 5760−5771.

“Smart" nanomaterials (such as polymers and core-shell nanoparticles) for potential applications in nanomedicine and nanophotonics were studied to elucidate, both, its morphology and the photochemical/photophysical processes taking place using selected probes. The performed time-resolved studies of PVK polymer nanoparticles (host) doped with Coumarine 153 (*C153*) and Nile Red (*NR*) showed multi-step (cascade) of energy transfer (ET) between PVK chromophores, *C153* and *NR*, allowing white light generation with a high quantum yield. The time constants of the involved ET events were obtained to optimize white light emission. The results also indicate how these processes are related to the dyes distribution (governed by Marangoni and Ouzo effects) inside the NPs at the time of its formation (Figure 2).

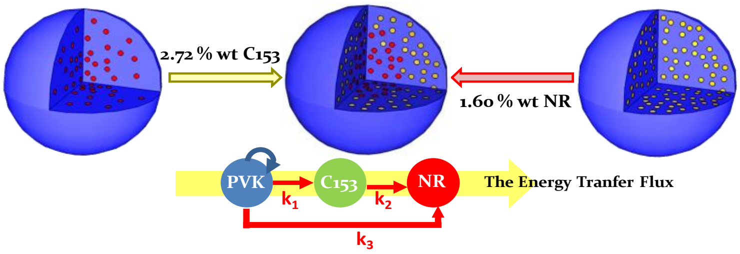

Figure 2. Illustration of the possible distribution of C153 (yellow spheres) and NR (red spheres) inside the PVK nanoparticles for one- and two doped systems. For a specific dopant concentration of C153 and NR (2.5 % wt de C153 y 1.6 % wt de NR, the multistep ET processes within doped PVK nanoparticles results in white light generation. These results were published in: 1) C. Martin, S. Bhattacharyya, A. Patra, and A. Douhal, “Single and Multiple Energy Transfer Processes within Dyes Doped Polymer Nanoparticles”, *Photochem. Photobiol. Sci.*, **2014**, *13*, 1241–1252 and 2) C. Martin, M.R. di Nunzio, B. Cohen and A. Douhal, “Location and Freedom of Single and Double Guest in Dye-Doped Polymer Nanoparticles”, *Photochem. Photobiol. Sci.*, **2014**, *13*, 1580–1589.

The inherent heterogeneity of the interactions inside the nanomaterials obscures other additional processes in the ensemble average measurements. Hence, the material should be characterised at single molecule/particle level in order to fully understand the mechanisms involved. *DY-630-MI* in core-shell silica nanoparticles were studied using confocal single molecule/particle fluorescence microscopy. The results showed that the inter-chromophores interaction within the particle is relevant to its emission spectra and lifetimes, and provide information to be used in improving the design, fabrication and development of more efficient nanosystems with potential applications in nanophotonics and fluorescent imaging technology.

- ***Studies relevant to catalysis: Nanocatalysis***

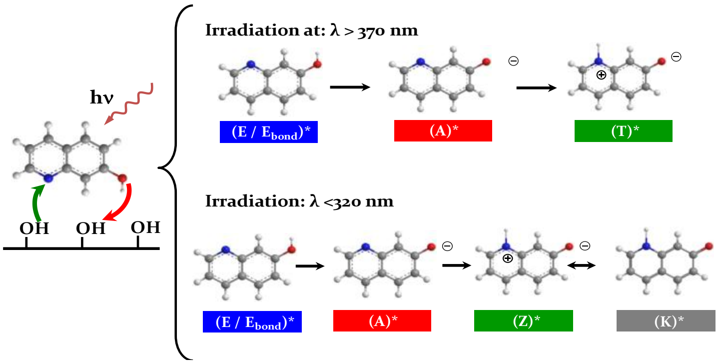

Figure 3. Illustration of the photoconversion routes of 7HQ/R-MCM41 Materials, showing how changes on the excitation wavelength controls de reaction pathway. This result was pusblished in: M. Gil, C. Martín and A. Douhal, "Femtosecond Dynamics and Photoconversion of a H-bonded Dye", *J. Phys. Chem. B* **2011**, *115*, 14687−14697.

In an attempt to understand the operation of nanocatalysts and catalytic supports at atomic and short time scales, probes (reactants) like 7-Hydroxyquinoline (7HQ) and DY630-MI were introduced in different mesoporous materials (MCM41 and derivatives), were studied using different spectroscopic techniques with temporal and spatial resolutions. The results gave a new understanding of the catalytic reaction mechanisms. For example, it was found that the interaction of 7-HQ with the silica-based materials is mainly through hydrogen bonding interactions between the dye molecules and the catalyst, which can be affected by the polarity and the electrostatic forces of the catalytic support. It was also found that the use of mesoporous materials may open the door to new photochemically controlled reaction paths, due to its effect on the tautomer equilibrium of 7HQ (Figure 3).

- ***Studies relevant to dye-sensitized solar cells (DSSCs): Nanophotonics***

The photodynamic behaviour of different dye-sensitized solar cells (DSSCs) was explored using femto to millisecond spectroscopy. The studies were focused on getting a better understanding of the properties of each component that conform the device and how they influence its performance. It was possible to draw in details (giving the time constant of the involved events) the working scheme of the DSSCs, and as a result to propose a basis to improve the DSSCs efficiency. To this end, DSSCs based on *TPC1* and *TH305* triphenylamines dyes as sensitizers) were studied. The results show different electron injection rates, which are dependent on the vibrational energy excess of the excited dye, the size and type of the semiconductor nanoparticles (of different band gaps), and electrolyte nature and additives. In addition to that, the recombination and regeneration processes were also explored giving a detailed and global picture of the total photodynamic cycle. Accordingly, mesoporous Ti-doped materials present an alternative to TiO_2 nanoparticles due to a lower electron recombination rate, while keeping similar electron injection values per titania atoms. Nevertheless, although these mesoporous Ti-doped materials have some advantages, the obtained low photocurrent indicates that further modifications are required before obtaining a viable complete device. Furthermore, the electrolyte is also an important part of a working DSSC device, where its composition has direct influence on the regeneration and electron injection processes (Figure 4). Recently, these and other DSSCs studies have made possible to publish an invited review in *J. Photochem. Photobiol., C.* (in press, DOI: 10.1016/j.jphotochemrev.2015.12.001).

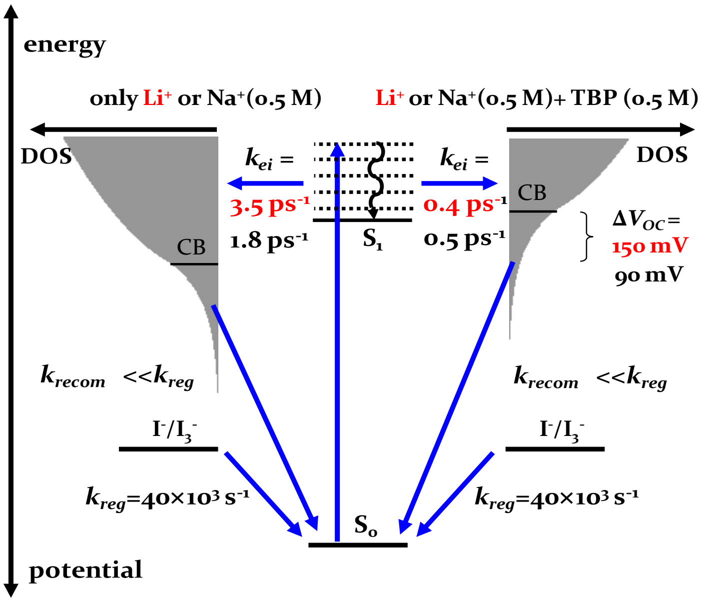

Figure 4. Schematic representation of electron Injection (rate constant, k_{ei}), electron recombination (rate Constant, k_{recom}), and dye regeneration (rate constant, k_{reg}) processes observed in the Complete DSSCs using TH305 as sensitizer. This result was pusblished in: M. Ziółek, C. Martin, L. Sun and A. Douhal, "Effect of Electrolyte Composition on Electron Injection and Dye Regeneration Dynamics in Complete Organic Dye Sensitized Solar Cells Probed by Time-Resolved Laser Spectroscopy", *J. Phys. Chem. B* **2012**, *116*, 26227-26238.

In summary, the combined use of steady-state observation, time-resolved (from femtosecond to the millisecond regime) and space resolved (single molecule fluorescence mcroscopy) optical spectroscopy techniques, from ensemble average to single molecule level, allowed to get a deeper understanding of the mechanisms and photophysical processes involved in the intimate interactions between the selected dyes and nanomaterials. A correlation between the photophysical properties of the complexes with the material morphology and structure, as well as the local environment is provided.

All of these results, relevant to important multidisciplinary topics in Nanomedicine, Nanocatalysis and Nanophotonics, resulted in 14 publications (in peer reviewed journals) and 35 (oral and poster) contributions in national and international conferences. Last but not least,, the development of this Ph.D thesis allowed also to strongly collaborate with national (Madrid, Valencia) and international (Japan, India, Sweden, USA) research groups providing the dyes or the nanomaterials.

Platinum Complexes and their Luminescent Assemblies

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Ph.D. Thesis, 2015; Research Adviser: Luisa De Cola

This Thesis comprises the synthesis and the photophysical characterization of a series of luminescent neutral Pt(II) compounds containing a tridentate dianionic N-donor chromophoric ligand and a monodentate ancillary moiety. The compounds exhibited notable change of the photoluminescence properties upon self-assembly due to the establishment of weak non-covalent intermolecular interactions – metal···metal and π- π.

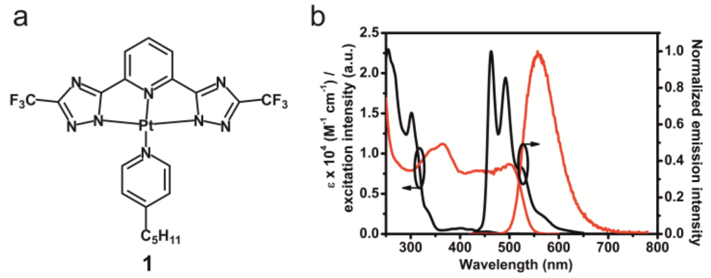


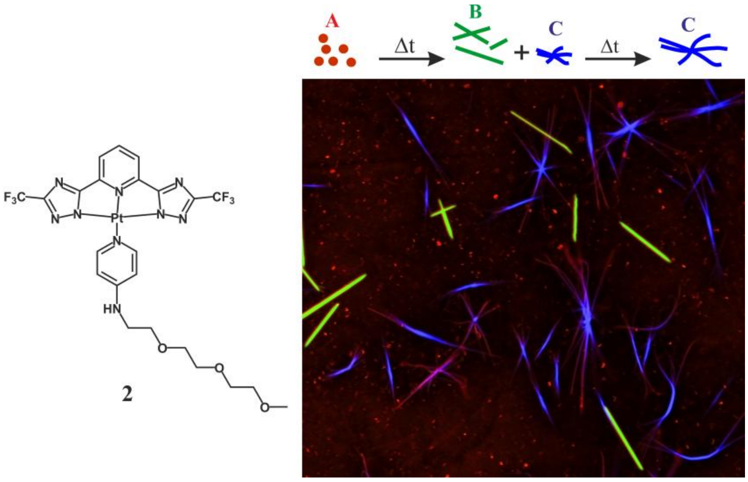
Figure 1. (a) Chemical structure of complex **1**. *(b) Absorption spectra and emission spectra (λ_{exc} =300 nm) obtained in $CHCl_3$ (5×10^{-5} M) at room temperature (black trace) and for the fibers obtained from 4 mg mL^{-1} acetone solution at λ_{em} = 630 nm and λ_{exc} = 300 nm (red trace). (c) Fluorescence microscopy image of the aligned fibers obtained from acetone under irradiation at λ = 400–440 nm. Scale bar = 100 μm.*

The absorption spectrum of complex 1 in dilute chloroform (CHCl3) solution (5x10-5 M) at room temperature is characterized by intense bands in the UV region mainly attributed to the intraligand (1IL) and metal-perturbed interligand charge transfer (1ILCT) states (figure 1b); while, upon photoexcitation, the sample display a weak blue luminescence attributed to an emissive excited state with mainly 3LC character. Interestingly, the slow evaporation of the solvent leads to the formation of yellow bright emissive microcrystalline fibers, which display an intense and featureless emission centered at λem,max = 559 nm with PLQY of 74% and a new band at lower energy (λ = 501 nm) in the excitation spectra (figure 1b) due to the establishment of highly directional metallophilic interaction (MMLCT). The self-assembled fibers show linearly polarized light absorption and emission.

The effects of the introduction of a single chiral center into the molecular have been investigated. Thus, two enantiomeric Pt(II) complexes bearing a chiral ancillary moiety ((S or R)-2-hydroxy-2-phenyl-N-(pyridin-4-ylmethyl)acetamide)) have been synthetized and chemically characterized. As a result, in diluted $CHCl_3$ solution ($5x10^{-5}$ M) the two enantiomeric complexes display identical photophysical properties and very much similar to those above mentioned for the parental complex **1**. When the complexes are molecularly dissolved it´s not possible to detect any circular dichroic signal (CD) (concentration range 10^{-6}-10^{-4} M) even if the ancillary chiral pyridine presents a clear CD signal. Upon drop-casting a 1.03 mg mL^{-1} THF solution of either the S- or the R- enantiomer onto a quartz substrate, formation of bright emissive fibers have been observed. Also in this case, the formation of a low-lying absorption band and the formation of a bathochromically-shifted broad emission is due to the establishment of ground state Pt···Pt metallophilic interactions, and can be attributed to a MMLCT band. Differently to what observed in solution, the self-assembled fibers display a strong CD signal and the sign of the Cotton effects is function of the enantiomeric configuration of the molecular structure of the platinum complex. Indeed, two mirroring CD spectra have been obtained for two enantiomeric complexes.

Then the self-assembly properties of the amphiphilic Pt(II) compound **2** have been comprehensively investigated. When the complex is molecularly dissolved in air-equilibrated 1,4-dioxane (0.1–$200x10^{-5}$ M) only a weak blue emission is detected with PLQY of about 1%. Upon flash-injecting a dioxane solution of **2** ($c = 2x10^{-3}$ M) into water – the latter acting as the non-solvent – a kinetically trapped metastable state (assembly **A**) has been formed. Such assembly is constituted by soft nanoparticles and displays a strong orange phosphorescence (PLQY = 84%) despite the air-equilibrated conditions due to the physical shield of the excited state located on the complex moieties. The strong bathochromically shifted emission band when compared to the emission in dilute dioxane solution is attributed to the establishment of Pt···Pt metallophilic interactions. It was found that by playing with the solvent/non solvent ratio and using an integrating sphere setup to investigate the overall changes in the photophysical properties, it has been possible to characterized and control a highly complex supramolecular landscape comprising two kinetic assemblies (namely **A** and **B**) and the thermodynamic isoform (namely, assembly **C**) as shown in figure 3.

At 95% water content, assembly **A** is stable for more than 10 hours without any detectable change in the photophysical properties. On the other hand, upon decreasing the amount of water by adding molecularly dissolved complex in pure 1,4-dioxane, which lowers the interconversion energy barrier, the system evolves to the thermodynamically favored isoform (assembly **C**). The solvent dependent kinetic as well as the large spectral changes over the different assemblies have allowed an unprecedented real-time visualization of the self-assembly processes (figure 2).



2

*Figure 2. Evolution of the assemblies of **2**.*

The establishment of Pt···Pt interactions between neighboring Pt(II) complexes to obtain dynamic labels for bioimaging applications has been investigated. The complexes **Tol-**

Pt-4OHpy and **CF_3-Pt-4OHpy** have been internalized in human cervical carcinoma, HeLa, cells. The emission spectra taken from the highly emissive spots have clearly demonstrated that for both complexes, the emission energy and shape correspond to those of the assembled systems. The emission of **Tol-Pt-4OHpy** is mainly observed in the cytoplasmic region while the **CF_3-Pt-4OHpy** is partially distributed in the cytoplasmic region, but bright aggregates are observed inside the nucleus, more precisely in the nucleoli. The low-lying ^{1}MMLCT absorption band makes them able to be excited also in the visible region down to λ_{exc} = 550 nm, while the monomeric counterparts display negligible absorption in this region. It has been demonstrated that the aggregation process is not only leading to the protection of the platinum complexes, preventing oxygen quenching, but also reduces photobleaching if compared to organic dyes, such as DAPI.

As already described the photoluminescent properties of this class of compounds strongly depends not only on the ligand-field splitting, but also on the intermolecular distance between the Pt(II) ions. It has been already demonstrated that Pt···Pt separation can be modulated also in solid state upon exposure to volatile organic compounds (VOCs) and mechanical stimuli which often results in a reversible change in the color of the materials upon mechanical stimulus (mechanochromism) and exposure to solvents vapors (vapochromism). In this respect the mechanochromic properties of bulk materials have been investigated and correlated with those at the nanoscale (single fibers). Different complementary techniques at bulk and nanoscopic level have been employed to monitor changes in the photoluminescent properties upon mechanical grinding (tribochromism) and by simple pressure (piezochromism). In particular, an AFM tip has been employed to modulate the mechanical stress from pure pressure to high friction in a single self-assembled fiber at the nanoscale. Moreover, it has been found that an AFM tip can be used to write submicron features with high fidelity on individual ribbons, which are individually used as homogeneous memory substrates.

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- "Nanopatterning of surfaces with mono- and hetero bi-metallic 1D coordination polymers: a molecular tectonics approach at the solid/liquid interface" M. El Garah, N. Marets, M. Mauro, A. Aliprandi, S. Bonacchi, L. De Cola, A. Ciesielski, V. Bulach, M. W. Hosseini, P. Samori J. Am. Chem. Soc., 2015, 137, 8450-8459.
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Photoactivatable Derivatives for Chemical and Biological Applications: Design, Synthesis and Mechanistic Investigation

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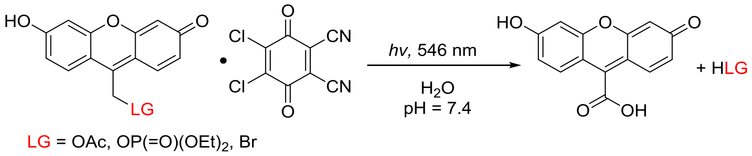
Ph.D. Thesis (in English), 2015, Research Advisors: Petr Klán, Burkhard König

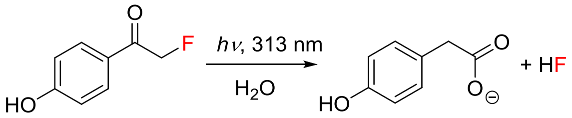
This thesis focuses on design, synthesis and mechanistic investigations of photoactivatable derivatives. It summarizes selected results of my Ph.D. research which have been published or submitted for publication.

In the theoretical part it summarizes basic information about selected topics relevant for the studied projects, such as photoremovable protecting groups, selected visible light absorbing chromophores, biologically relevant caged ions and small molecules, and visible light photocatalysis.

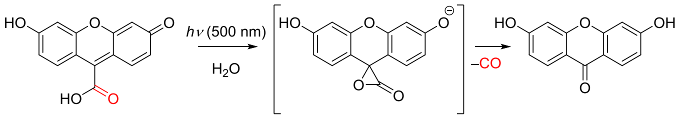
The part Results and Discussion is divided into eight chapters. The first chapter deals with a xanthene-based photoremovable protecting group (PPG). We managed to prepare the first PPG capable to release phosphates, carboxylates and halides by the action of green light (λ_{max} ~ 520 nm)[1].



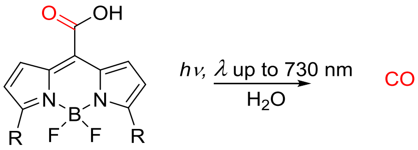
The second part introduces 4-hydroxyphenacyl fluoride[2], a caged fluoride, which can be efficiently released (Φ ~ 84%) by UV-light irradiation. The mechanism of fluoride release has been studied by picosecond pump-probe spectroscopy. The released fluoride was used for etching of silicon surfaces followed by AFM.



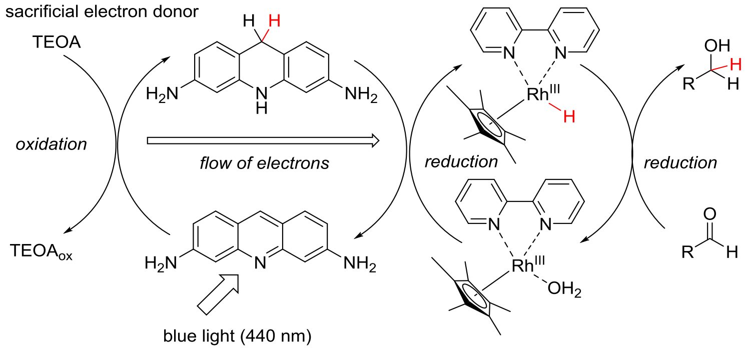
The third project describes the first metal-free carbon monoxide-releasing molecule (CORM) activatable by visible light based on the xanthene structural motif.[3]



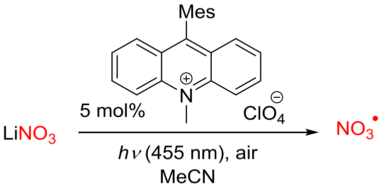
The fourth chapter improves the concept of visible light absorbing CORMs by using BODIPY-based chromophores.[4] These molecules can release CO upon irradiation by light at up to 730 nm and were successfully tested in both *in vitro* and *in vivo* biological experiments. The mechanism of the photodegradation was carefully studied.



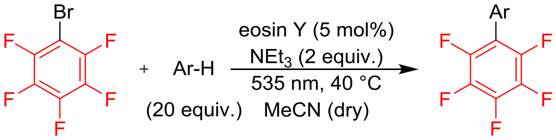
The fifth chapter deals with a photocatalytic system for reduction of carbonyl compounds.[5] It uses proflavine as a photocatalyst, rhodium mediator, and triethylamine as a sacrificial electron donor. The system selectively reduces aldehydes over ketones. Both electronic and steric effects are responsible for the selectivity which is kinetically controlled.



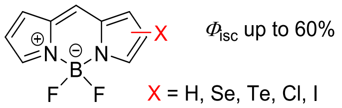
The sixth project describes a novel photocatalytic method for generation of the nitrate radical which is further used for some synthetic applications.[6] The mechanism of generation of the nitrate radical by photooxidation of the nitrate anion has been studied in detail.



The seventh chapter discusses a new method for generation of fluorinated aryl radicals which are used in the synthesis of fluorinated biaryls as well as in late stage functionalization of some complex molecules.[7] The transient spectroscopic study has revealed the mechanism of the aryl radical formation.



The last project focuses on the synthesis of selanyl- and tellanyl-substituted BODIPY derivatives.[8] The quantum yield of intersystem crossing (up to 60%) has been measured by transient spectroscopy. These derivatives can be used as triplet sensitizers.



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3) "Fluorescein Analogue Xanthene-9-Carboxylic Acid: A Transition-Metal Free CO Releasing Molecule Activated by Green Light." L. A. P. Athony, T. Slanina, P. Šebej, T. Šolomek, P. Klán, Org. Lett. 2013, 15, 4552-4555.

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8) "Internal Heavy-Atom Effect in 3-Phenylselanyl and 3-Phenyltellanyl BODIPY Derivatives Studied by Transient Absorption Spectroscopy." J. Al Anshori, T. Slanina, E. Palao, P. Klán, 2015, submitted

Fluorescent protein design for superresolution microscopy: exploring the power of protein engineering

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KU Leuven

Fluorescent proteins (FPs) have revolutionized cellular and molecular imaging beyond compare, as was illustrated with the Nobel prize in Chemistry in 2008. Six years later, in 2014, the Nobel prize in Chemistry was awarded for the development of superresolution fluorescence microscopy, an ensemble of techniques that allow the molecular basis of life to be visualized beyond the diffraction limit in optical microscopy. For the larger part, live-cell applications of these superresolution techniques crucially rely on the performance of FPs in live samples. These two fields (FP development and superresolution imaging) are still active and highly relevant today.[1,2] In this thesis, significant contributions have been made to both.

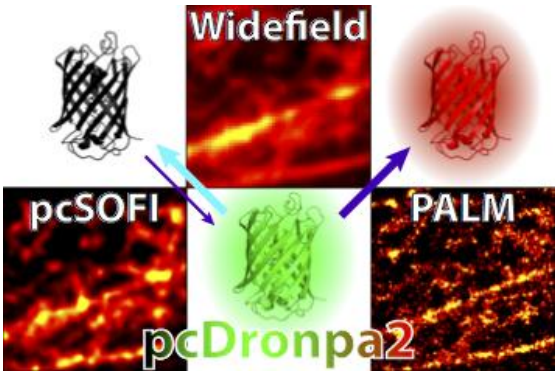

Figure 1. pcDronpa2 can, thanks to its photoswitchable and photoconvertable properties, be used for multimodal superresolution imaging, combining pcSOFI with PALM.

In the first part of this dissertation, two new FPs were semi-rationally engineered: NijiFP3 and pcDronpa2.4 Both belong to the still scarcely populated class of FPs with both photoswitching and photoconversion properties.5 Not only did our thorough spectroscopic and structural characterization6 lead to new insights into the mechanistics of FPs, they also proved to be the probes of choice for eg. pulse-chase PALM imaging7 and multimodal superresolution imaging (**Figure 1**).

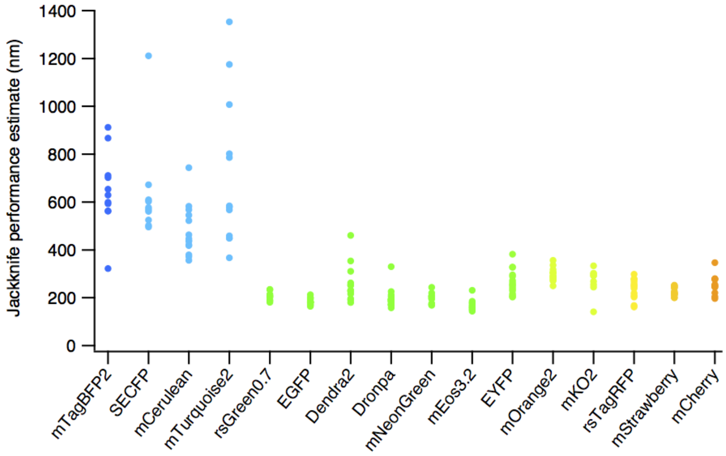

Figure 2. Performance estimate in pcSOFI for each of the 16 labels used in this study. Every dot represents a pcSOFI experiment.

In the second part of this thesis, we made contributions to the field of superresolution imaging, focusing on photochromic stochastical optical fluctuation imaging (pcSOFI).[8] This robust and easily-accessible technique is an ideal method for obtaining two- to threefold improvement in resolution in widefield fluorescence imaging. Our contributions cover a discussion of the use of photoswitchable FPs for superresolution imaging and a detailed step-by-step guide to pcSOFI on living cells.[9] Additionally, using Fourier transform analysis, we managed to calculate a performance estimate associated with a given pcSOFI image.[10] Using this criterion, we compared 16 different FPs, spread over the entire visible range, as to their performance in pcSOFI (**Figure 2)**. Surprisingly, we identified EGFP, the most widely used FP and considered non-photoswitchable, to be an extremely well-performing probe for pcSOFI. This broadens the applicability and accesibility of pcSOFI significantly.

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TiO_2 Gas Phase Photocatalysis: from Morphological Design to Plasmonic Enhancement

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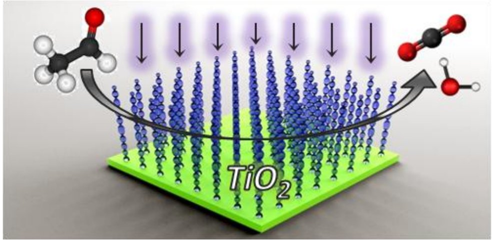
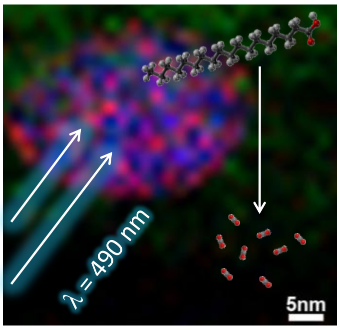
Center for Surface Chemistry & Catalysis, University of Leuven, Belgium
Ph.D. Thesis (in English), 2014; Research Advisors: Silvia Lenaerts and Johan Martens

In this Ph.D. thesis TiO_2 photocatalysis as an air cleaning technology is investigated in all its facets. The first main achievement is the development of a cost and material-efficient immobilization method and testing procedure. The reactor design, based on glass bead supports packed around a lamp in a cylindrical glass reactor tube, offers the advantages of good immobilization, efficient light utilization, intimate contact with gaseous pollutants and a catalyst weight gain by a factor of 25. A cost effectiveness analysis (CEA) is carried out as a multidisciplinary tool to evaluate commercial photocatalysts in terms of their activities as well as material costs.
Next, more fundamental insight is gathered in the driving factors of gas phase photocatalysis. Structural properties such as large surface area and an accessible pore system seem to dominate over electronic properties. This knowledge is exploited in the development of spacious TiO_2 thin films, prepared by depositing a conformal TiO_2 layer onto sacrificial carbonaceous templates by means of atomic layer deposition (ALD). Upon heat treatment, the template is removed, TiO_2 is crystallized into the anatase phase and the TiO_2 layer is transformed into an interconnected network of nanoparticles. These films exhibit superior photocatalytic acetaldehyde degradation compared to a commercial reference film. In order to test the films a single pass flatbed photoreactor was conceived, that was characterized using computational fluid dynamics (CFD).



A final achievement on the fundamental photochemical level is the extension of TiO_2 photoactivity from the UV range of the spectrum toward the visible light region of the spectrum. This is done by exploiting surface plasmon resonance (SPR) effects of gold-silver alloy nanoparticles. First, a theoretical model is established to predict the SPR wavelength of such alloy nanoparticles, based on the combined effects of size and alloy composition. Next, these alloy nanoparticles are used to fabricate plasmonic photocatalysts with tunable visible light photoactivity. This is showcased for stearic acid degradation under 490 nm LED illumination, corresponding to the solar wavelength range with maximum intensity output.



In conclusion: gas phase photocatalysis is studied using a multidisciplinary approach. Various improvements are proposed on both reactor and catalyst level, taking into account technological and experimental, but also theoretical and financial aspects.

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Theoretical and Experimental Study of Reactive Intermediates with Emphasis on the Development of New Photoactivatable Compounds

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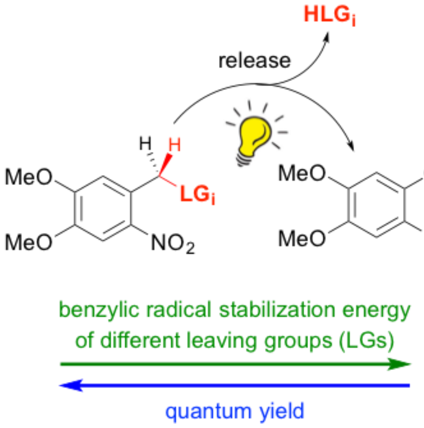
Ph.D. Thesis, 2014; Research Advisers: Professor Petr Klán and Professor Thomas Bally

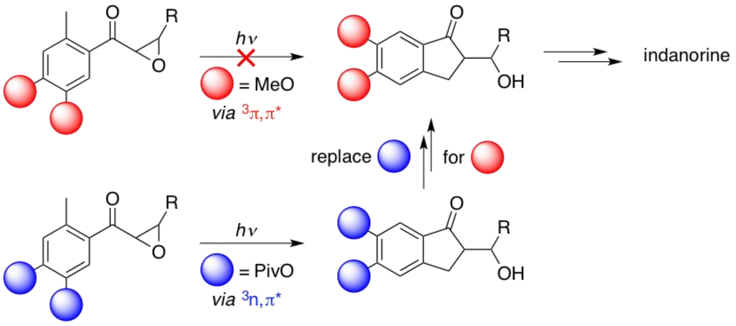
This dissertation focuses on investigating the formation and electronic properties of diradicaloid intermediates generated by means of light absorption or by thermal activation upon pyrolysis, and their reactivity, which determines the outcome of their subsequent chemical reactions.

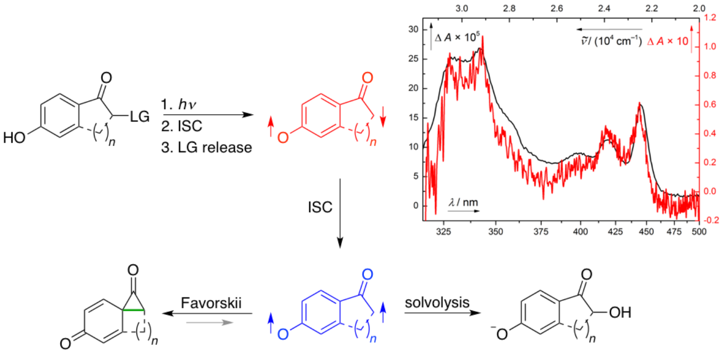
In the first part of the thesis, the mechanisms for the cleavage of small molecules from photoactivatable (or "caged") compounds that span several important and widely used photoremovable protecting groups (PPGs) are studied by quantum-chemical calculations that support results of time-resolved spectroscopy measurements, previously published data or serve to predict the outcome of experiments. It is identified that the diradicaloid species formed in the course of the photolysis of these PPGs strongly affect the efficiency or the chemoselectivity of the photochemical reaction.

In particular, it was found that the quantum yield for the release of a leaving group (LG) from *o*-nitrobenzyl (oNB, see Figure belo) "caged" compounds varies greatly with the nature of this leaving group, for reasons that have never been well understood. It was identified that the barriers for the primary photochemical reaction, the excited state hydrogen transfer (ESHT) to the nitro group, and the nonradiative processes on the excited singlet and triplet energy surfaces determine the quantum yields. The excited state barriers vary with the nature of LG and decrease with increasing exothermicity of the photoreaction, in accord with Bell–Evans–Polanyi principle, a tool that has never been applied to a nonadiabatic photoreaction. This allowed to propose a general model for the reactivity of oNB "caged" compounds that was put to a semiquantitative test by comparing calculated ESHT rate constants and theoretical quantum yields with experimental data. Thereby, it was clarified why the quantum yield for "uncaging" oNB derivatives may depend on the excitation wavelength and the enigmatic kinetic isotope effect that was found previously could be explained. Finally, it is showed that a simple ground state predictor, the radical stabilization energy, correlates with the computed ground and excited state reaction energies and excited state barriers.

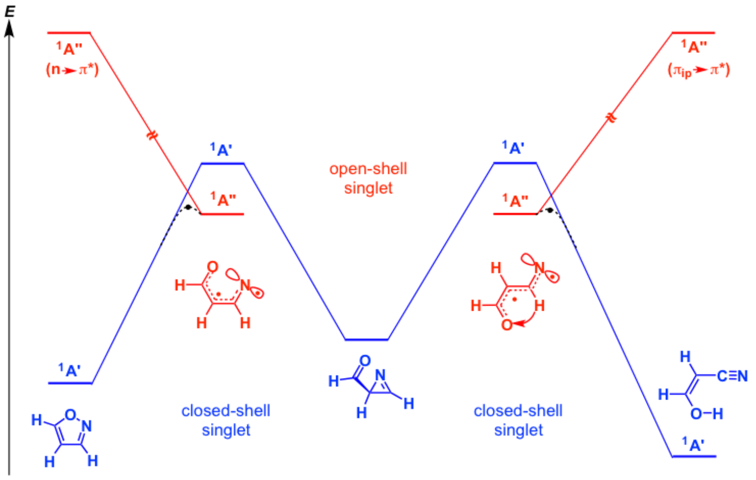


Next, the photoenolization in *o*-alkyl aromatic ketones was studied. It was found that irradiation of *o*-methylbenzoyl oxiranes results in the relatively efficient formation of β-hydroxy functionalized indanones which structurally resemble biologically active pterosines. The mechanism of the reaction was investigated by quenching experiments, Stern-Volmer analysis, and quantum yield measurements. It was identified that electron donating methoxy substituents alter the chemoselectivity of the reaction by retarding the ESHT step in the triplet state. A strategy based on an electronic state switching to control the chemoselectivity of the photochemical process was proposed. A suitable “electronic state protecting group” was selected, which resulted in a complete change in the selectivity, and in the efficient formation of the desired indanone derivative. These predictions were achieved by using readily available density functional theory calculations which were done prior to any laboratory experiments. This strategy enabled accomplishing the total synthesis of indanorine, an antiproliferative agent, involving a key photochemical step in 39% total yield.





Finally, the investigation of the effect of ring strain on the rearranging p-hydroxyphenacyl moiety was used to probe the involvement of various intermediates, especially the putative Favorskii-like cyclopropanone and oxyallyl-like diradicals, in the course of the photoreaction. It is demonstrated that the reactivity of singlet oxyallyl diradicals that are formed via intersystem crossing from their triplet isomers dictates the selectivity of the formation of final products. Ring strain plays a decisive role in their kinetic stability and determines also the rate of intersystem crossing. The present analysis, based on high-level quantum chemical calculations, is in excellent agreement with the results of pump-probe and laser flash photolysis experiments. Eventually, the first example of a singlet oxyallyl diradicaloid that cannot form the corresponding cyclopropanone nor the isomeric allene oxide was identified. This singlet oxyallyl diradicaloid is, instead, trapped by water to form a solvolysis product. The observations provide a comprehensive overview of the role of oxyallyl diradicals in reaction mechanisms in general, and offer a new strategy to stabilize open-shell singlet diradicals.The second part of the dissertation is devoted to the study of carbonylvinylnitrenes which serve as pivotal intermediates in the high-pressure pulsed pyrolysis of isoxazoles, the products of which were trapped in Argon matrices at 15 K and studied by means of high-resolution IR spectroscopy. Thereby, the formation of a new product, 3-hydroxypropenenitrile, was observed. Methyl substituents in the 3- and 5-positions in the parent isoxazole led to formation of other rearrangement products, i.e. 2-acetyl-3-methyl-2H-azirine at moderate pyrolysis temperatures, and 2,5-dimethyloxazole at higher temperatures. These findings were rationalized by means of multireference quantum chemical calculations that provided a comprehensive picture of the reaction mechanism, a picture which is in excellent accord with the experimental findings.



However, the fleeting nature of the carbonylvinylnitrenes preclude their direct spectroscopic characterization. Therefore, a design to stabilize these intermediates by blocking or hampering most of their decay pathways is proposed and supported by calculations. Thus a tricyclic benzisoxazole that leads to a relatively stable nitrene intermediate, which should be detectable under suitable experimental conditions, was identified.

The carbonyl-nitrene diradicals formed by breaking the N–O bond in the designed benzisoxazoles have surprisingly low open-shell (OS) singlet–triplet energy gaps. By modifying the structure of these nitrenes a design to a nitrene with nearly isoenergetic OS singlet and triplet states is presented. Nevertheless, all the nitrenes possess *non-disjoint* non-bonding molecular orbitals (NBMOs), which precludes to invert the energies of OS singlet and triplet states. A topological change in the nodal properties of one of the NBMOs was then achieved and the OS singlet–triplet energy gap for the corresponding nitrene was computed to be negative, *i.e* it is proved that a nitrene with an OS singlet ground state is possible.

In summary, the understanding of the formation, the electronic properties based on topology of the frontier molecular orbitals, and the fate of the reactive intermediates studied in this dissertation provides a basis to design new and more efficient photoactivatable compounds that are capable of releasing a protected species upon visible light exposure desirable in the biological/clinical applications.

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The Role of Vibrations in Photoinduced Electron Transfer in Molecular Systems

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Photosynthetic organisms harvest light from the sun and convert it into useful chemicals. The key underlying mechanism in this elegant process is electron transfer (ET), which allows converting light into energy-rich charge separated states. Potential technological applications ranging from information storage to efficient solar energy conversion have impelled vigorous fundamental research in ET processes in the last sixty years. Phenomenal progress has been made, yet many fundamental questions remain open.

One of the most intriguing aspects of ET is its dramatic dependence on the coupling of nuclear and electronic degrees of freedom (vibronic coupling), which can dictate the rates and efficiencies of ET in systems ranging from simple molecules to biological organisms. The goal of this thesis is to investigate the role of vibronic coupling in ultrafast solution-phase light-induced ET in transition metal complexes relevant to solar energy conversion.

In order to probe vibronic coupling in a time-dependent manner, one must use spectroscopic tools capable of correlating the motions of electrons and nuclei on an ultrafast timescale. Recent developments in nonlinear multidimensional electronic and vibrational spectroscopies allow monitoring both electronic and structural motion with unprecedented time and spatial resolution. The primary methods used in this thesis are variants of the frequency-domain Transient 2-Dimensional Infrared (T-2DIR) pulse sequence, which combines electronic and vibrational excitations in the form of a UV-Visible pump, a narrowband (12 cm^{-1}) infrared (IR) pump and a broadband (400 cm^{-1}) IR probe.

In the first instance, T-2DIR is used to directly compare vibrational dynamics in the ground and relaxed electronic excited states of Re(Cl)(CO)3(4,4'-diethylester-2,2'-bipyridine), a prototypical charge transfer complex used in photocatalytic CO_2 reduction. The experiments show that intramolecular vibrational redistribution (IVR) and vibrational energy transfer (VET) are up to an order of magnitude faster in the triplet charge transfer excited state than in the ground state. These results show the influence of electronic arrangement on vibrational coupling patterns, with direct implications for vibronic coupling mechanisms in charge transfer excited states.

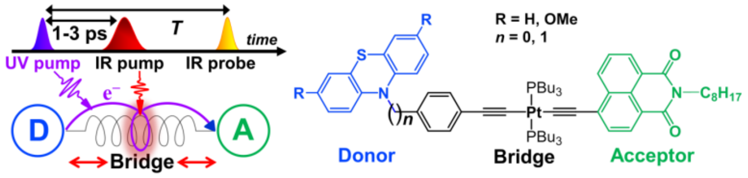

Figure 1. Summary of IR-control experiments, whereby exciting bridge-localised vibrations during charge separation leads to radical changes in photoproduct yields.

In the second instance, the importance of vibronic coupling is unambiguously demonstrated in Donor-Bridge-Acceptor complexes based on a Pt(II) *trans*-acetylide design motif (Figure 1). By selectively exciting bridge-localized vibrations within a few picoseconds of electronic excitation, the Donor-Acceptor charge separation pathway can be switched off, with all excess energy redirected towards the formation of a long-lived intraligand triplet state. A series of control experiments reveal that this effect is mode specific: it is only when the high-frequency bridging C≡C stretching mode is excited that radical changes in photoproduct yields are observed. These experiments therefore suggest that one may control condensed-phase photophysics and photochemistry by stimulating structural motion along chosen reaction co-ordinates using low-energy infrared light.

These studies add to a growing body of evidence suggesting that vibronic coupling is a gateway to controlling the light-induced function of molecular systems. Achieving such control would represent a major breakthrough for charge transfer-based applications such as solar energy conversion and molecular electronics.

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Photophysics and photochemistry of singlet oxygen precursor chromophores: insights from static calculations and molecular dynamics

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Ph.D. Thesis (in English), 2014; Supervisors: Prof. Manuel Yañez and Dr. Inés Corral

Despite reactive oxygen species (ROS and $^1O_2$) have been identified as responsible for the skin photo-oxidation processes, their oxidative properties have been also used with therapeutically anticancer effects. Thereby, tons of efforts have been done towards finding chromophores able to produce $^1O_2$ after being treated with light and then destroy tumoral cells. Understanding, the mechanism by which this chromophores produce $^1O_2$ and ROS is fundamental for the design of new systems that ideally will only present beneficial properties but not detrimental effects.

Two types of chromophores have been studied along this thesis providing important information about their mechanism of action. DNA bases where a carbonyl oxygen atom has been substituted by sulfur, thiobases, have been used as therapeutical photosensitizers during decades. However, detrimental effects have been discovered in patients after years of treatment with these bases (high skin cancer incidence) and have led to the search of new generation of photosensitizers. These thiobases generate $^1O_2$ after being activated with light and in presence of molecular oxygen in the media.

The second type of studied systems is endoperoxides, aromatic systems carrying an O-O bridge. These systems have been proposed as prototype of effective photosensitizers, which are able to produce $^1O_2$ even in the absence of molecular oxygen in the media.

In the above context this Thesis aims to elucidate the photodeactivation mechanism of the mentioned systems both from static high-level multiconfigurational calculations and semiclassical dynamics. This approach allows knowing at molecular level all energetically possible competing relaxation mechanism and evaluating their relative importance according to the outcome of the time resolved picture provided by the dynamics.

Moreover, the combined static and dynamic analysis allows a more reliable interpretation of the experimental results of the systems considered in this thesis by estimating photoproduct yields and time scales for different processes.

Finally, the photophysical and photochemistry of purine free base have also been investigated aiming to provide insight on how the nature and position of different substituents affect the absorption properties and the photostability of these systems.

Preparation and characterization of rare earth metal modified TiO_2

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Ph.D. Thesis (in Poland), 2014; Research Adviser: Adriana Zaleska

1. Introduction

In recent years, environment friendly contaminant disposal methods and conversion method of organic and inorganic substances are intensively investigated. Titanium dioxide represents an effective photocatalyst for water and air purification and for self-cleaning surfaces. Additionally, it can be used as antibacterial agent because of strong oxidation activity and superhydrophilicity. TiO_2 shows relatively high reactivity and chemical stability under ultraviolet light (λ<387 nm), whose energy exceeds the band gap of 3.3 eV in the anatase crystalline phase. In this regard, the development of photocatalysts exhibiting high reactivity under visible light (λ>400 nm) should allow the main part of the solar spectrum, even under poor illumination of interior lighting, to be used. Several approaches for TiO_2 modification have been proposed: metal-ion implanted TiO_2, non-metal doped-TiO_2, composites of TiO_2 with semiconductor having lower band gap energy and sensitizing of TiO_2 with dyes. The photocatalytic mechanism is initiated by the absorption of the photon hv_1 with energy equal to or greater than the band gap of TiO_2 (~3.3 eV for the anatase phase) producing an electron-hole pair on the surface of TiO_2 nanoparticle. An electron is promoted to the conduction band (CB) while a positive hole is formed in the valence band (VB). Excited-state electrons and holes can recombine and dissipate the input energy as heat, get trapped in metastable surface states, or react with electron donors and electron acceptors adsorbed on the semiconductor surface or within the surrounding electrical double layer of the charged particles. After reaction with water, these holes can produce hydroxyl radicals with high redox oxidizing potential. Depending upon the exact conditions, the holes, OH radicals, O_2^-, H_2O_2 and O_2 itself can play important roles in the photocatalytic reaction mechanism.

In order to enlarge the utilization ratio of the solar light, nanosized TiO_2 modified with rare earth metals was synthesized. Rare metal (RE) doping of TiO_2 is a new promising method to enhance activity under visible light due to up-conversion effect. According to available literature, up-conversion luminescence agents could transform the visible light into the ultraviolet light to satisfy the genuine requirements of TiO_2 photocatalysts. The simplified mechanism of TiO_2 excitation by up-conversion luminescence agent is presented in Figure 1.

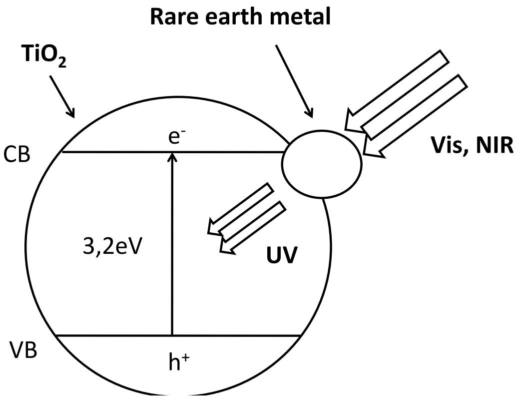

Figure 1. Simplified mechanism of TiO_2 excitation by up-conversion luminescence agent

2. Aim of the work

The aim of this work was to understand the effect of dopant type and content (Er^{3+}, Yb^{3+}, Eu^{3+}, Pr^{3+}, Ho^{3+}, Nd^{3+}) and the effect of co-doping (Er^{3+}/Yb^{3+}, Er^{3+}/Nd^{3+}, Eu^{3+}/Nd^{3+}, Eu^{3+}/Ho^{3+}, Au/RE^{3+}) on the structure, optical and luminescence properties, and their relation with the photocatalytic properties under visible light. Prepared samples were characterized by X-ray diffraction (XRD), X-ray photoelectron emission spectroscopy (XPS), UV-Vis absorption measurement, BET surface area analysis and luminescent spectroscopy. The photocatalytic properties have been investigated by employing of the photodegradation of phenol and acetic acid in aqueous phase and toluene in gas phase as a model pollutants. The most important part of the research was complementary characteristics including the effect of irradiation wavelength on apparent quantum efficiency (action spectra analysis) which helped to understand the excitation mechanism of prepared samples and mechanism discussion. Based on these studies, from action spectrum analysis, can be calculated which fraction of irradiation absorbed by a photocatalyst did, indeed, take part in the photocatalytic reaction.

3. Selected results

- Pr/TiO_2

Pr-TiO_2 nanoparticles were prepared by the sol-gel method and had anatase structure. Photocatalysts based on TiO_2 and doped with praseodymium caused an increase of photocatalytic activity under visible light irradiation. It was observed that the dopant affects the surface area and crystal size of TiO_2 powder samples. Photocatalytic activity depends on rare earth ion precursor concentration used during the preparation. TiO_2 doped with 0.25 mol% of praseodymium showed the highest photocatalytic activity under visible light. After 60 min of irradiation, 25 % of phenol was degraded.

- Au-Er, Au-Nd, Au-Ho, Au-Eu, Au-Pr/TiO_2

Preliminary results have shown that photodegradation of toluene in the air over the Au-RE-TiO_2 using light emitting diodes is possible. However, it was found that co-doping of TiO_2 with rare earth metal and gold nanoparticles inhibited photoactivity both, under UV and Vis irradiation, compared to pure TiO_2. The highest activity under visible light from among Au-RE-TiO_2 was observed for the sample doped with Er^{3+} or Pr^{3+}. Reducing the concentration of gold precursor from 2 to 1 mol.% during synthesis, resulted in decrease of photocatalytic activity. It was observed that TiO_2 surface modification with rare earth metal and gold nanoparticles caused an decrease of the surface area of modified TiO_2 powders. Since plasmon band near 550 nm typical for gold nanoparticles was observed, sol-gel preparation method followed by chemical reduction of gold ions did not enhance photoactivity under visible light.

- Nd-Er, Nd-Eu, Eu-Ho/TiO_2

Co-doping by Nd^{3+}/Er^{3+}, Nd^{3+}/Eu^{3+} or Eu^{3+}/Ho^{3+} pairs increases the surface area of TiO_2 due to inhibition of crystal up growth and favors photocatalytic activity under visible light comparing to pure titanium dioxide. XPS analysis indicated that all rare earth metals are present in the form of oxides (RE_2O_3) on TiO_2 surface. The highest activity under visible light in both model reactions (phenol and acetic acid oxidation in aqueous phase) was observed for the sample prepared by introducing 1 mol% of Eu^{3+} and 1 mol% of Ho^{3+} ions during the preparation process. It contained a relatively higher fraction of the reduced species in form of Ti^{3+} (3.9 % of Ti^{3+} and 96.1 % of Ti^{4+}) and a lower amount of carbon species on TiO_2 surface comparing to other samples.

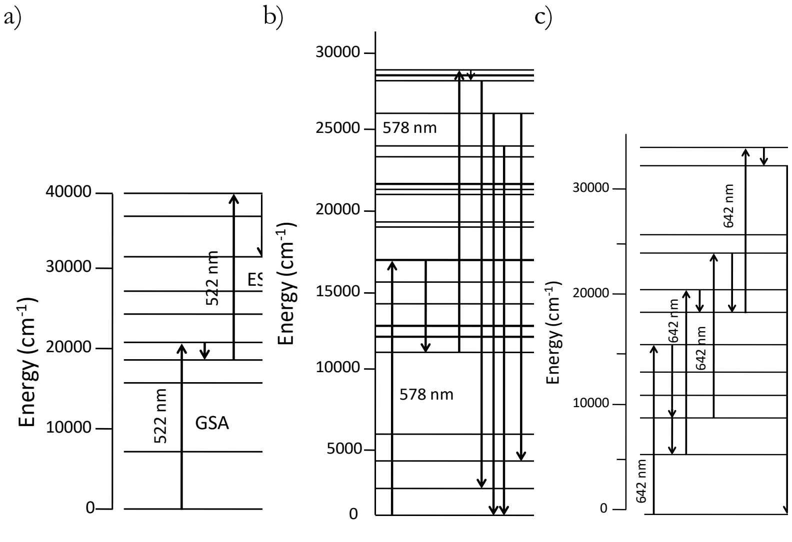

Figure 2. Simplified energy-levels diagrams of and excitation path for the up- conversion emission at ultraviolet light a) Er^{3+} under 522 nm excitation, b) Nd^{3+} under 578 nm excitation, c) Ho^{3+} under 642 nm excitation; GSA - ground state absorption, ESA - excited state absorption.

Luminescence measurements showed emission only in the case of the samples containing Eu3+ ions. Spectroscopic properties of Eu3+ doped sample indicated highly quenching properties of the host material, multisite distribution of the dopants and high asymmetry of the surrounding Eu3+-site local environment. Simplified energy-levels diagrams of and excitation path for the up- conversion emission at ultraviolet light is presented in Figure 2b and c.

The up-conversion effect for the samples doped with Eu^{3+}, Er^{3+}, Ho^{3+} and Nd^{3+} was not observed. Action spectra analysis for high active samples showed that RE^{3+}-doped TiO_2 could be excited under visible light in the range from 420 to 450 nm.

- Er, Yb, Er-Yb/TiO_2

Visible light-activated anatase system was obtained by doping with Er^{3+}, Yb^{3+} and Er^{3+}/Yb^{3}. XPS analysis revealed that erbium and ytterbium were present in the form of oxides. Figure 2a illustrates the excitation of Er^{3+} under visible light, where the absorption of 524 nm photons promotes Er^{3+} from ground state to $^2H_{11/2}$ excited state. The up-conversion process can be achieved through the chains of ground state absorption (GSA) and excited state absorption (ESA). For TiO_2 materials doped with Er^{3+} or Yb^{3+}/Er^{3+} after excitation by 978 nm laser beam, low intensive up-conversion emission was observed. Yb^{3+}-TiO_2 containing 1 mol% ytterbium, exhibits the highest photocatalytic activity under visible light ($\lambda > 450$ nm) irradiation. Action spectra analysis showed that RE^{3+}-doped TiO_2 could be excited under visible light in the range from 420 to 475 nm. The primary mechanism for the visible light sensitization was probably due to the availability of higher adsorption sites, increase of the BET surface area, decrease of the crystallite size and prevention of electron–hole recombination. Luminescence properties of Er/Yb-TiO_2, as well as XRD analysis, indicates incorporation of dopant ions into TiO_2 crystal structure creating oxygen vacancies and surface defects.

Based on the experimental results, the proposed mechanism of photocatalytic oxidation of phenol in presence of Yb-TiO_2 nanoparticles is shown in Figure 3.

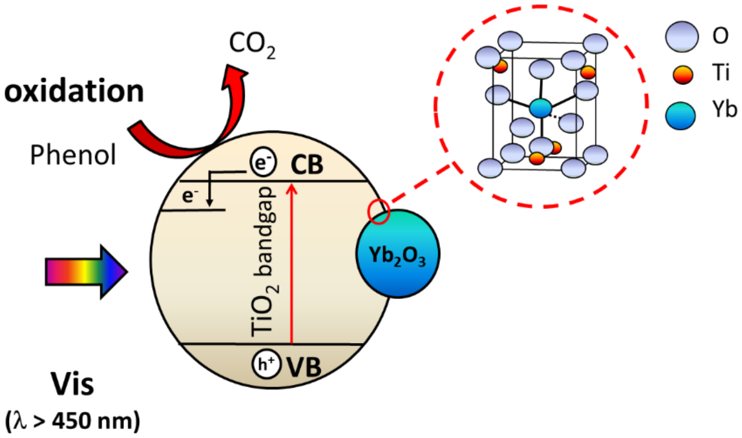

Figure 3. Schematic mechanism of photocatalytic oxidation of phenol under visible light irradiation in presence of Yb-TiO$_2$ nanoparticles

4. Conclusions

We have obtained a highly under visible light active TiO$_2$ system by modifying with rare earth metals compared to the bare TiO$_2$ and P25 (commercial TiO$_2$). The sample showing the highest photoactivity is in form of anatase, its surface area equal to 125 m^2/g, average crystals size is 13 nm and contain 0.07 at% of Yb$_2$O$_3$ and about 20 at% of carbon in the surface layer. 3 h of visible light irradiation resulted in 89% of phenol degradation. XPS analysis revealed that rare earth metals were present in the form of oxides, but luminescence properties measurements indicated that RE^{3+} may also be substituted by Ti^{4+}, creating abundant oxygen vacancies and surface defects. It was observed that the dopant type and concentration affects the surface area and crystal size of TiO$_2$ powder samples. For TiO$_2$ materials doped with Er^{3+} or Yb^{3+}/Er^{3+} after excitation by 978 nm laser beam, low intensive up-conversion emission in visible light was observed. The up-conversion emission in UV light was not observed. The primary mechanism for the visible light sensitization was probably due to availability of higher adsorption sites, red shifts, increase the BET surface area, decrease the crystallite size and prevention of electron–hole recombination.

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CONFERENCE REPORTS

XXVIth IUPAC Conference on Photochemistry April 3rd-8th 2016 in Osaka, Japan

The XXVIth IUPAC conference on photochemistry in April 2016 was organized by Professor Tetsuro **Majima** from Osaka University together with a large group of local organizers. He had chosen a remarkably impressive place to gather, the Osaka City Central Public Hall, an eye-catching building in the center of Osaka featuring pale red bricks and a bronze dome roof. Built as a public hall for local citizens and completed in 1918, it has become as much a symbol of Osaka – just in walking distance from the impressive Osaka Central Station as well as from Osaka Castle. Approximately 600 participants from all parts of the world and all areas of photochemistry, photobiology and photophysics met in Osaka. This conference was accompanied by a pre-symposium in Hiroshima (by Prof. Manabu **Abe**) and two post-symposia in Kyushu and Osaka (by Prof. Yoshio **Hisaeda** and Prof. Hiromi **Yamashita**) and included also the 12th Korean-Japan binational symposium on "Frontier Photoscience" (KJFP-2016).

The cornerstones of this symposium were 8 plenary and 11 invited lectures together with **291** oral (including 49 young researcher and 36 student oral presentations) and **187** poster contributions. As a spectacular starting point of this conference, Akira **Fujishima** from the Tokyo University of Science, Japan, referred about "Photocatalysis and CO_2 reduction". The groundbreaking work by Honda and Fujishima in the late 60th and 70th of the last century on the photocatalytic activities of titanium dioxide initiated the enormous research activities in the fields of semiconductor photocatalysis, photocatalytic water splitting, oxidation technologies in surface and water purification with an impressive potential in day life applications. Richard A. **Mathies** from the University of California at Berkeley, USA, presented his results on "A coherent picture of photobiology and photochemistry" where he demonstrated that vibrational dephasing and return to the lowest excited states as described by Kaska´s rule is no longer occurring for ultrafast reactions of excited states at the femtosecond time scale, e.g. the photoisomerization of the cis-retinal chromophore in the visual pigment rhodopsin that occurs in about 50 femtoseconds.

Thomas **Carell** from the University Munich, Germany, referred about "Time resolved IR and crystallographic studies of DNA photodamage and repair" and described the newest results on the complex mechanisms of repair processes of photoinduced DNA lesions such as cyclobutane or 6-4 single bond lesions. He explained the differences in green plant photorepair enzymes and mammalian repair by nucleotide excision. Cornelia **Bohne** from the University of Victoria, Canada, gave her talk on "Mechanistic insights from supramolecular studies on the binding of guests with cucurbit[n]urils" and described a sophisticated study on rate constants of host-guest interactions of photoreponsive molecules with natural bile acids and cucurbiturils as host molecules.

Harry **Anderson** from Oxford University, England, referred about "Excited state energy delocalization in synthetic porphyrin nanorings" where he described the synthesis of linear and cyclic oligometalloporphyrins by a template route that allowed the approach to hitherto unthinkable compounds with extended energy delocalizations in their excited singlet states. Dario M. **Bassani** from the University of Bordeaux, France, delivered a presentation of "A supramolecular approach to controlling the behavior of excited states" where he described the directionality and predictability of hydrogen-bonding as tool with which chromophores can be pre-oriented prior to photoexcitation in solution and in the solid. The products obtained from supramolecular photoreactions may exhibit

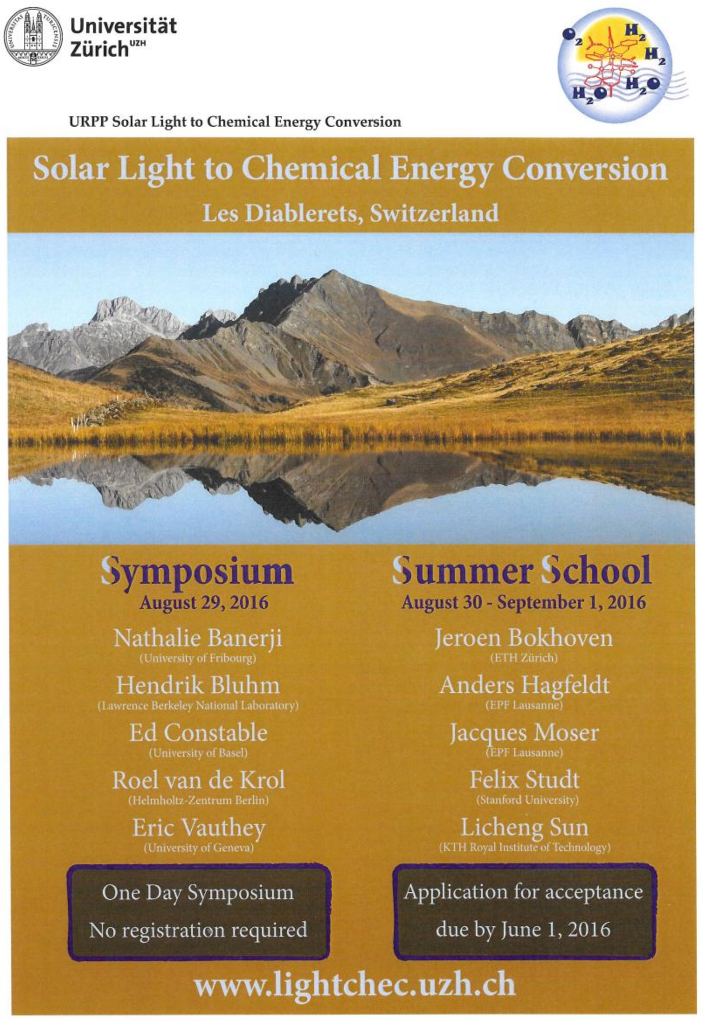
affinity for a chosen template, thereby providing a route to substrate-induced receptor synthesis.
Can **Li** from the Dalian Institute of Chemical Physics, China, referred about "Photogenerated charge separation in artificial photosynthesis systems" and presented the research progress on solar fuel productions from artificial photosynthesis, namely photocatalysis and photoelectrocatalysis (PEC) processes with the emphasis on the photogenerated charge separation. Nicola **Armaroli** from the National Research Council in Bologna, Italy, gave a talk on "Photoactive materials for energy conversion" and described the strategies to optimize the luminescence output, color and stability of Ir(III) and Cu(I) complexes, along with the possibility to switch from metal complexes to hybrid organic-inorganic materials and fully organic triplet luminophores

The next IUPAC conferences on photochemistry will be organized in Dublin, Ireland in July 2018 by Prof. Miguel **Garcia**-**Garibay** and in Amsterdam, The Netherlands, in July 2020 by Prof. Fred **Brouwer**. This conference series is alternating in odd years with the "International Conference on Photochemistry (ICP)" that is organized in 2017 in Strasbourg. These two conference series are clearly the path makers of international research in photochemistry and will be linked in future more strongly in order to make this structure a more powerful stage for exchange of research results and a tool to foster this important area in natural sciences.

Osaka, April 2016,

Axel G. Griesbeck

ANNOUNCEMENTS



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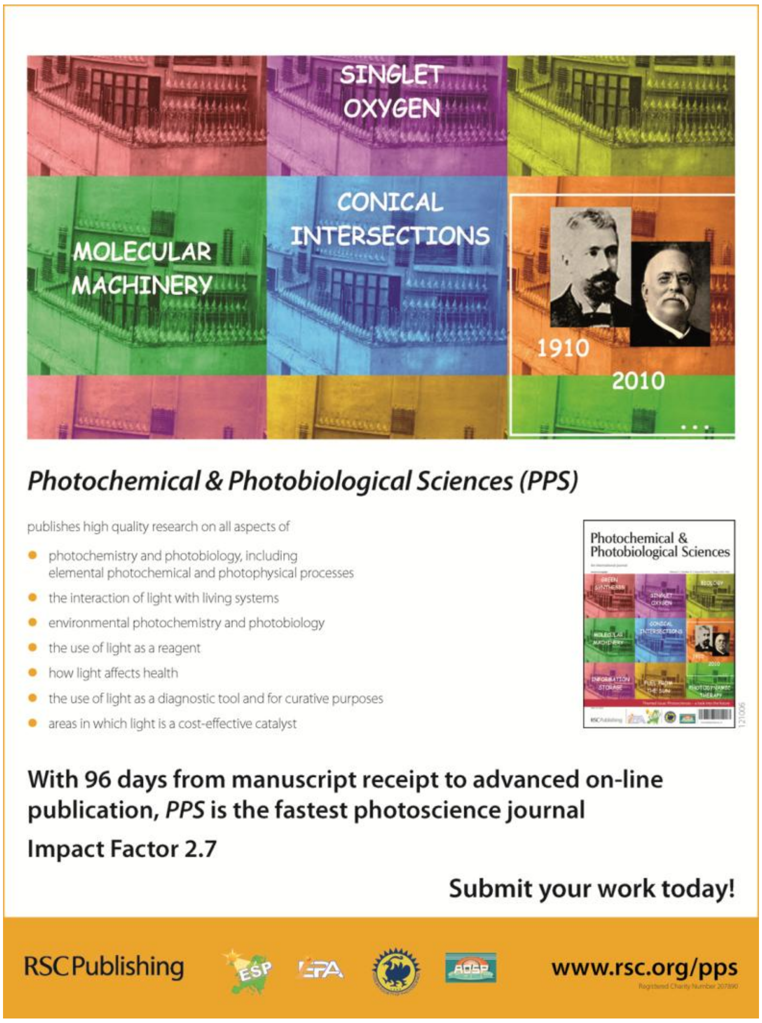

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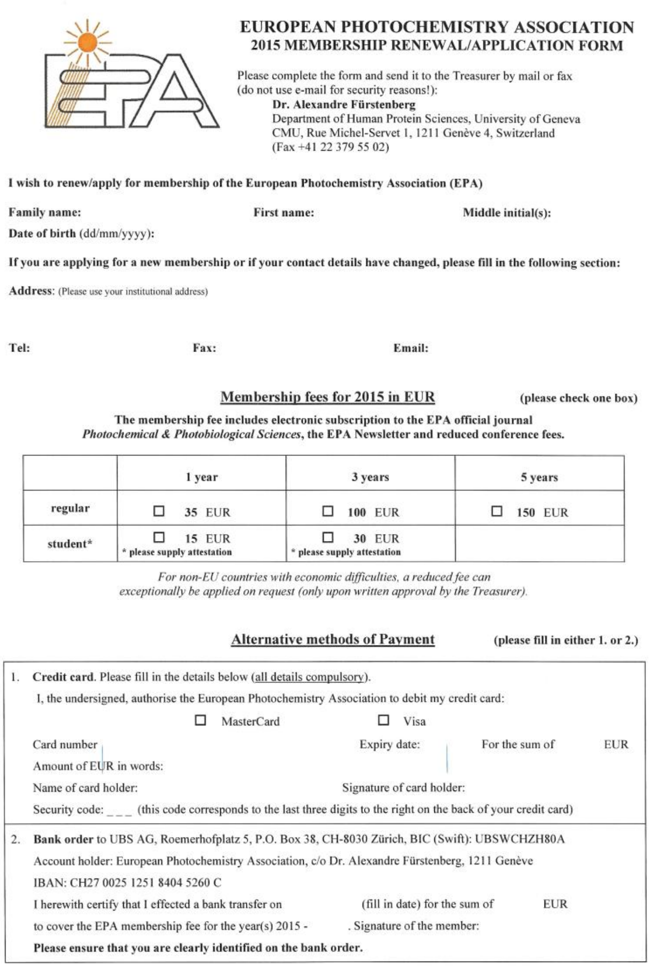

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