

# **NEWSLETTER**

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**Newsletter Editor: Dr. Norbert Hoffmann** 

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# **EPA EXECUTIVE COMMITTEE**



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# New Information Technologies

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# **EDITORIAL**

## President's Letter

Dear EPA members,

This is the last letter from the president written by me. I have to say I'm sorry to get away from this role. I would have many things to propose and implement, and I will no longer be able to do it. I can only hope that someone will collect my legacy and go on.

But beyond the complaints, it is only fair that you realize what has happened since about a year ago. A meeting of the Ownership Board of Photochemical and Photobiological Science was held in Cambridge on 8th May 2019 at the Royal Chemical Society. At that point, item 8 on the agenda was the item "Amendment to royalty: request to raise from 2% to 5%". The request for an increase in royalties came from photobiologists. It was a legitimate request that was based on the fact that the increase in royalties would have allowed to increase the promotion activity of their discipline. The Royal Chemical Society's response on this point was not there. We were promised that an answer would come by the summer. On 10th July 2019 we receive an email from the Royal Chemical Society informing us that RSC was beginning "a new strategy covering the next 5 years, to allow us to re-focus on our core publishing activities". On this basis, we were informed of the decision not to renew the contract for the publication of Photochemical and Photobiological Science at the expiry of the contract, that is, starting from January 2021.

This new situation produced an important change to our entire activity. On the one hand it was necessary, together with the European Society for Photobiology, to find a new publisher for our journal, a publisher that was able to guarantee serious development for the journal, on the other hand it forced us to block all our activities. We had in mind to invest part of the revenues from royalties in a project to support and revitalize the photochemistry summer schools and to build an advanced photochemistry school. This project could not be carried out in the absence of economic security which suddenly disappeared.

Our decision was to create a Task Force that would follow the problem of finding a new publisher for *Photochemical and Photobiological Science*. The Task Force was made up of Julia Perez Prieto, Alberto Credi, Werner Nau, and Alexandre Fürstenberg. Now I have to thank all of

them warmly for the work they have done for the well-being of the community. Contacts were made with many potential publishers, but the solution that promised to be the most viable was that with Springer Nature.

At the moment I signed the contract with the new publishing house (Springer Nature). A new challenge is appearing which appears promising and full of positive potential.

I hope that all members will be able to support our magazine, just as I hope that the new president will be able to make the best use of the potential offered by the new situation.

Maurizio D'Auria Università della Basilicata

### **PUBLICATIONS**

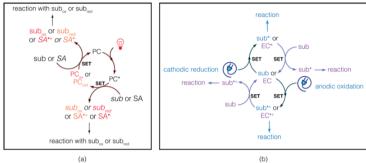
# Electrophotocatalysis: the combination of electron and photon in synthetic organic chemistry

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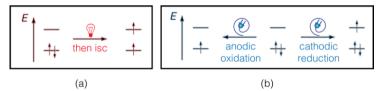
Electrochemistry and Photoredox catalysis: two distinct methods entwined by their radical nature

Electronic excitation significantly changes the reactivity of chemical compounds. Over the last years, photoredox catalysis and electrocatalysis have been studied and mentioned alongside each other although both research fields use single-electron transfer as activation so as to generate very reactive radical intermediates (Figure 1).



**Figure 1.** Comparison between photoredox catalysis (a) and electrocatalysis (b) in organic chemistry. Both methods use SET (single-electron transfer) as activation. Oxidation and reduction take place in a same catalytic cycle in photoredox catalysis whereas oxidation and reduction occur (spatially) in two different catalytic cycles. PC = photocatalyst, sub = substract, SA = sacrificial agent, EC = electrocatalyst.

Both techniques considerably enrich the range of chemical reactions available in organic synthesis. Indeed, single electron transfer is a very powerful tool to induce chemical transformations. In the case of photocatalytic reactions, the energy of the absorbed photons is used to promote an electron to an upper orbital (Figure 2 (a)). The resulting electronic configuration, so called "excited state", has stronger reducing and oxidizing properties than the molecule at its ground state. On the other hand in the case electrocatalytic reactions, a potential is applied in the solution and affects the redox properties of the electrocatalyst which will then react with the substrate (Figure 2 (b)).



**Figure 2.** Simplified orbital diagram for photochemical excitation (a) and electrochemical excitation (b).

Photoredox catalysis requires that the catalyst used is the only photoreactive species at irradiation wavelength, in order to avoid parasitic photochemical reactions. The range at which the catalyst absorbs light is therefore restricted, and should preferentially absorbs near -or- visible-light. Beer-Lambert's law prevails. A too high concentration or a too high extinction coefficient (at the irradiation wavelength) will prevent the whole system to be irradiated, and will therefore affect the yield of the chemical transformation (such a limitation can be surpassed and is very studied in continuous flow photochemistry reactors¹). The optimal amount of photons used has also to be determined, and the photoreactivity of the photocatalyst has to be known and mastered. Furthermore, one should keep in mind that the highest potential achieved by photoredox catalysis is generally not as powerful as the one of the strongest oxidants/reductants in conventional chemistry. However, the use of stronger classical oxidants/reductants requires drastic chemical conditions which any chemist tries to avoid.

In electrocatalysis, the choice of the voltage has a to be precise in order to avoid any parasitic reaction. This implies to perfectly know the potential of the targeted reaction. The efficiency of each electrochemical reaction depends on the ability of the current to flow through the system and is quite independent of the concentration of the substrate. Therefore, the choice of the solvent is crucial. This latter has to be able to dissolve electrolytes in order to increase the conductivity of the whole system. Virtually, very high reductive/oxidative potentials are reachable depending on the lab equipment. As photoredox catalysis and electrocatalysis are complementary, numerous reactions have been carried out using these two methods independently.<sup>2</sup>

Electron or photon? Different pathways towards the synthesis of similar structures. One of the most ancient and well-known reaction in organic electrochemistry is Kolbe reaction (1848).<sup>3</sup> This latter corresponds to a decarboxylative dimerization of two carboxylic acids or carboxylate ions via anodic oxidation (Figure 3).

Figure 3. General Kolbe electrolysis.

This reaction offers the advantages of its versatility: numerous compounds containing carboxylic acid function can be used to make

this dimerization, as long as the molecules involved don't bear functions that can be oxidized. Among the major drawbacks of Kolbe reaction, regioselectivity is hard to handle as all the carboxylic functions of an unique molecule can be subjected to oxidation, leading to the formation of side-products. Also, platinum anode use is mandatory to avoid formation of R<sup>+</sup> carbocations in the mixture, enabling the so-called pseudo-Kolbe reaction.<sup>4</sup> This last disadvantage limited Kolbe electrolysis to be used in an industrial-scale.

More recently, photoredox catalysis versions of Kolbe reaction have been developed, in particular in the group of MacMillan in the United States.<sup>5-11</sup>

The use of photon enables a better regioselectivity and widen the scope of this reaction. As C-C coupling is still an important research axis, photochemical methods suggest another strong alternative to common organometallic processes as depicted in Figure 4.

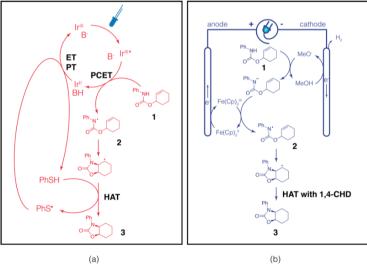
$$\left.\begin{array}{c|cccc} \text{BF}_3K & \bigvee \text{MgX} & \bigvee \text{B(OR)}_2 & \bigvee \text{ZnX} \\ \\ \bigvee \text{SiR}_3 & \bigvee \text{SnR}_3 & \bigvee \text{PdL}_2X & \bigvee \text{Cu} \end{array}\right\} \text{ replaced by } \bigvee \text{COOH} \text{ in photoredox catalysis}$$

**Figure 4.** Common organometallic reactions for C-C coupling can be replaced by a photoredox Kolbe reaction method.

Some photoredox catalysis reactions can now be made with only the use of electrochemistry.<sup>2</sup> Knowles team successfully perform C-N coupling via olefin hydroamination using an Iridium photocatalyst (Figure 5, red).<sup>12</sup> One year later, Xu group proposed an analogue reaction using only electrochemical activation (Figure 5, blue).<sup>13</sup>

**Figure 5.** Synthesis of Pyrrolidinones, oxazolidinones, imidazolinones and thiazolidinones derivatives by photoredox catalysis (red) or organic electrochemistry (blue).

Even though scope of the both reaction are akin, some differences in the mechanism can be noticed (Figure 6). Whereas a PCET (proton-coupled electron transfer) is involved in the photoredox catalysis version with 1, followed by a HAT (Hydrogen Atom Transfer) via benzenethiol (Figure 6 (a)), cathodic reduction leads to an electron transfer on methanol to produce MeO as a base, with formation of dihydrogen gaz (Figure 6 (b)). Methanoate allows the formation of amidure via acid/base reaction which then undergoes an oxidation by Fe(Cp)<sub>2</sub><sup>III</sup> to produce radical 2. This latter can recombinate on the double bond and a sacrificial hydrogen-donor, 1,4-CHD gives product 3. It is important to underline there, in contrary of the case of photoredox catalysis, hydrogen-donor is not regenerated.



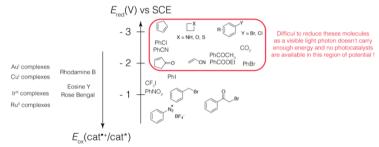
**Figure 6.** Photochemical (a) and electrochemical (b) olefin hydroamination of compound **1**. B is for base (NBu<sub>4</sub>OP(O)(OBu)<sub>2</sub>) and 1,4-CHD is 1,4-cyclohexadiene, ET and PT denotes "electron transfer" and "proton transfer" respectively.

Figure 6 shows an important point that has been developed previously: reduction and oxidation take place in a same catalytic cycle in photoredox catalysis. In organic electrochemistry, these two processes take place in different catalytic cycles. These both methods each succeed in being incorporated in synthesis of molecules of interest like

progesterone acid derived carbamate or androgesterone receptor modulator.

# Merging electricity and light: towards powerful reductants and oxidants

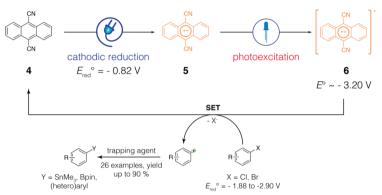
Absorption of light by a molecule enhances its redox properties: excited-state is characterized by a decrease of oxidant potential and an increase of reduction potential. Many efforts are carried out to develop new coordination/organometallic and dyes to always have stronger redox potentials to apply in synthesis. Nevertheless, some compounds are still virtually unreachable to be functionnalized in photoredox catalysis due to their large reduction or oxidant potential as shown in Figure 7.



**Figure 7.** Examples of some compounds with high reduction potential. Comparison with oxidation potential of few metallic complexes and organic dyes. A similar comparison could be done in oxidation range.

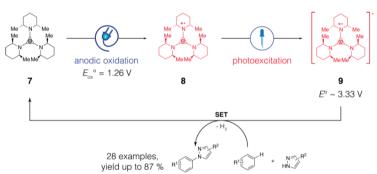
Technically, electrochemistry is able to easily reach any molecule reduction/oxidation potential with common laboratory equipment. Optimization of reaction conditions has already leaded to important improvements in the field of organic electrochemistry, allowing for its rebirth. Combining advantages of using photon as a reagent and electrochemistry, very recent works have been made in a new era of organic chemistry synthesis: electrophotocatalysis. In this latter, electrochemistry and photochemistry are combined to allow catalyst for having great reduction or oxidation potential. Early 2020, Lin and Lambert research groups proposed an electrophotocatalyst 6 issued from anthracene-9,10-dicarbonitrile 4, with an extreme reducing potential of -3.20 V vs SCE. This potential is enough to reduce aryl

halides as presented in Figure 8, whereas it was not practicable with known photocatalysts (Figure 7).



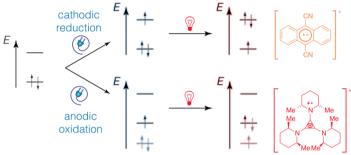
**Figure 8.** Reductive electrophotocatalysis with **6**. Towards activation of C-X aryl bonds. Potentials are given vs SCE, SET means "single-electron transfer".

Electrophotocatalysis is not limited to reduction. Lambert's group elaborated oxidative electrophotocatalysis with catalyst 9.<sup>26</sup> This latter bears an oxidative potential around 3.33 V vs SCE making him able to activate C-H aryl bonds (Figure 9). DDQ was also employed as electrophotocatalyst for activation of C-F aryl bonds.<sup>27</sup>



**Figure 9.** Oxidative electrophotocatalysis with **9**. Towards activation of C-H aryl bonds. Potentials are given vs SCE.

In both cases, electrochemistry allows for shifting absorption spectra to visible region, enabling the use of visible light to carry out the photoexcitation. In oxidative electrophotocatalysis example, triazoles derivatives were also successfully subjected to dimerization with arene molecules. Using TD-DFT, Lambert's group characterized the low-lying excited electronic states of the electrophotocatalysts employed. It was then shown that the exceptional redox potentials of the these latters was due to a HOMO-SOMO level inversion after photochemical excitation (Figure 10).



**Figure 10.** Inversion of HOMO-SOMO in electrophotocalysis for the two examples presented.

Electrophotocatalysis is actually paving a new way in organic synthesis where advantages of electrochemistry and photochemistry are used towards functionalization of molecules unattainable by each method independently. Numerous efforts are still ongoing to understand fundamentally this combination of these two modes of activation.

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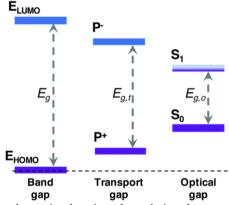
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# HOMO-LUMO and optical gap *in-situ* investigation of thin and ultra-thin organic layers

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The use of organic molecules in hybrid devices (*i.e.*, heterogeneous junctions) requires a fine tuning of their electronic properties in view of, on the one hand, matching the energy levels of the electrodes and, on the other hand, exploit their potentialities as photosensitive elements. The former requirement needs details of the HOMO-LUMO gap of the used molecules; the letter prescribes the application of optical spectroscopic techniques that are surface sensitive to few layers of molecules deposited onto the functionalized electrode. Figure 1 summarizes this picture.



**Figure 1.** A schematic showing the relation between the HOMO-LUMO and optical gap. A detailed knowledge of these gaps, the difference being due to the exciton binding energy, allows a fine tuning of the molecular transport properties within a hybrid electronic device.

The main difference between the HOMO-LUMO and the optical gap is due to the formation of an organic exciton, whose binding energy shrinks the band gap. The HOMO-LUMO gap can be directly measured by exploiting photoemission (PES) techniques.2 UV-PES, where the light produced by a He-lamp shines the sample and the produced photo-electrons are analysed by a hemispherical detector, is able to highlight features of the normally-filled states. Conversely, inverse-PES (IPES) is a suitable technique to directly acquire data from the "normally empty" states. In this case, a focused electron beam of few eV is sent to the sample. During the electron relaxation, light is emitted and revealed by a detector (channeltron). PES and IPES are typical surface-sensitive techniques due to the mean electron free path in condensed matter. Conversely, the optical gap measurement requires optical spectroscopies where the UV-vis light usually penetrates inside the sample for hundreds of nanometers. The reflected beam (considering opaque samples) is thus a bulk characteristic instead of a property of the organic film grown on the surface. For this reason, it is important to subtract the bulk contribution from the collected signal (modulation techniques). Historically, two main apparatus have been developed: surface differential reflectivity (SDR)<sup>3,4</sup> and reflectance anisotropy spectroscopy (RAS)5,6, which use different strategies to enhance the surface contribution in the reflected light. SDR simultaneously acquires and compares the reflected signal from the sample (organic film/substrate) and a pristine substrate, while RAS exploits linearly polarized electric fields to enhance the organic film contribution when an isotropic substrate is used. Both SDR and RAS can be placed outside the preparation chamber and the light can shine the sample through special viewports.

In our facilities, PES, IPES, SDR and RAS are coupled together in view of a full characterization of organic thin and ultra-thin films. In particular, the latter are prepared in an organic molecular beam epitaxy (OMBE) chamber (base pressure in low 10<sup>-10</sup> mbar) connected to the main chamber through a gate valve. In this way, the samples are always preserved from atmospheric contamination and the HOMO-LUMO *versus* the optical gap can be performed on freshly prepared samples.

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## PILLS OF HISTORY

# 10<sup>th</sup> photochemistry meeting in the Gastein valley

Stephan Landgraf, EPA Austria

#### Foreword of Horst Kisch

In the seventies and eighties of the last century, the West German "Fachgruppe Photochemie" (photochemistry discussion group) of the "Gesellschaft Deutscher Chemiker" (German chemical society) made joint meetings with the neighboring countries France and Switzerland. During my time as chairman from 1991 to 1993, I thought that type of symposium should be held also with Austria and Italy. But I was so heavily engaged in the unification with the photochemistry section of the Chemical Society of the DDR (former German Democratic Republic) that I postponed the realization of my idea. But it emerged again in 1996 at the XVIth IUPAC Symposium on Photochemistry in Helsinki when I sat together with Gottfried Grabner (University of Vienna) and Franco Scandola (University of Ferrara), chairmen of the corresponding national EPA sections. The colleagues accepted the idea, and we decided to organize together a symposium in Austria in the form of a Gordon Conference but only with one type of thirty minutes contributions and without invited lectures. All fields of photochemistry should be covered with a special focus on the participation of young researchers. After identifying Badgastein in the Austrian Alps as conference location I chaired the first German-Austrian-Italian Photochemistry Symposium (GAIPHOS) from March 1st to 5th, 1998. It was proposed that the next meeting shall be organized in Italy. About 85 participants enjoyed vivid discussions during the morning and evening sessions. The personal atmosphere was nicely demonstrated when Ugo Mazzucato (University of Perugia) in his closing address thanked me with a bear hug.



Figure 1. Conference photo of the GAIPHOS meeting 1998 [1].

### Foreword of Axel Griesbeck

Several years after the first international Badgastein photochemistry conference, time was high for another trial and, due to the turn of the Millennium, the second conference was termed "Perspectives of Photochemistry in the New Millennium".

The conference was organized as a tetranational meeting bringing together young and experienced photochemists from Switzerland, Austria, Hungary, and Germany. As the regional organizers served Thomas Bally, Günter Grampp, Laszlo Horvath, and Axel Griesbeck. In the comfortable Hotel Europäischer Hof (sic) in Badgastein, 70 participants met for discussing photochemistry in the morning and evening sessions and for hiking/skiing in the afternoon. This 4-day meeting covered nine plenary lectures, 18 oral, and 38 poster contributions. Major funding came from the Swiss Society of Photochemistry and the German Chemical Society. The conference did not end without a strong commitment to continue in a 2 years interval.

### Foreword of Stephan Landgraf

Merging the ideas of GAIPHOS (Gordon conference like meeting) and PPNM (biannual schedule of such a meeting), the future of the Gastein photochemistry conferences was born. Still, an organizer had to be found.

In 2005 on the way back from the Gordon research conference on photochemistry (Bryant University, Smithfield, RI, July 10 to 15), I met Axel Griesbeck at Boston Logan international airport in terminal E. As all European participants, we had to wait in the terminal for the flight connection in the late afternoon. Due to lack of lockers, we had to wait for five hours and more at the airport. So, we started to discuss many topics. During the discussion, Axel came up with the idea of a photochemistry meeting in the Gastein valley in 2006. I agreed to organize it, but it was not clear which countries should join next time. After some time, I proposed to make it accessible to (almost) all European countries at least those in the center of Europe. Therefore, we suggested the name Central European Conference on Photochemistry, short CECP.

In order to optimize the quality of such a conference we elaborated some rules:

- We choose some key countries with many photochemists.
- Each key country sends one chairperson.
- The chairpersons change each time.
- Each chairperson selects one invited plenary lecture.
- All chairpersons evaluate the applications for oral contributions.
- The chairpersons do not present an oral contribution on their own.
- The program orientates on the evaluation list starting from the best talk.
- The local organizer does not participate in any evaluation.
- Posters are accepted if the topic is on photochemistry.
- Poster sessions have plenty of time for discussion.
- Posters stay at the board for the whole meeting time.
- Poster sessions are organized in an even/odd number presenting fashion.

- The best oral and the best poster presentation from a young participant are honored by a prize.
- The conference should connect strongly west and east Europe.
- Students have a very low conference fee.
- Participants from east Europe pay a lower fee, too.
- Less favored regions should be supported by some grant.
- We set-up a web page and manage most things electronically.

Later a company exhibition (2008) and short industry presentations (2016) were added.

We were quite satisfied with the results of the discussion. Let's make it every two years. The original idea was to change the local organizer every two years, but ...

In order to find a proper location for a larger meeting, I went back into the Gastein valley in the summer of 2005. Based on an internet search I went from one possible location to the next. When arriving at the *Hotel Europäischer Hof* they told me to enter a new prize class. This was the definite end of this location. After approximately 10 possible facilities, I entered the congress center of Bad Hofgastein. The people from the tourist office responsible for the center were very friendly and offered an all-inclusive price, which was surprisingly low. The center is in the middle of the village and many accommodations are within walking distance to the conference. After some discussions, I decided to try this location for the next meeting in 2006.

### History of the Gastein photochemistry meetings

After previous joint meetings organized by the EPA section of Italy and Germany (D-F Strasbourg 1994, D-CH-F Konstanz 1996, I-CH Como 1987, I-F Aix-en-Provence 1989, I-A Krems 1993) it was time to enter the Alps. In order to organize this Horst Kisch from Erlangen together with Gottfried Grabner from Vienna and Franco Scandola from Ferrara and built the organizing committee of the 1st GAIPHOS (German Austrian Italian Photochemistry Symposium). The meeting was held at the *Hotel Europäischer Hof* in Bad Gastein, province of Salzburg, Austria.

The meeting began on Sunday, March 1, 1998, with the registration and the dinner. The next day the morning session started at half-past eight with oral contributions by S. Monti, H.K. Biesalski, A.R. Holzwarth, S.E. Braslavski, K. Rechthaler, and U.-W. Grummt. The session closed at noon. A five hours break gave all participants time for physical activities, e.g. skiing. At five p.m. the meeting continued with presentations from A. Albini, D. Döpp, T. Bach, and A. Griesbeck. After the dinner at the hotel, the poster session started. The first 20 of 41 posters were presented and had to be removed on Tuesday. The schedule of the other two meeting days was the same and the second poster session was on Wednesday evening.

On Tuesday the presentations were given by H. Hening, L. Flamigni, A. Vogler, H. Yersin, A. Credi, and C. Chiorboli in the morning and U. Rempel, J. Keck, S. Scheider, and K.A. Zachariasse in the afternoon. On the last meeting day, the presentations were given by G. Kaupp, J. Mattay, H.-G. Löhmannsröben, H.-J. Deyerl, L. Dähne, and T. Gensch in the morning and K.H. Drexhage, H. Görner, C. Kryshi, and L. De Cola in the evening.

On Thursday, there was only a morning session with I.R. Bellobono, R. Bauer, G. Grampp, D. Velic, L. Spanhel, and G. Hörner. The meeting was closed at noon after 36 oral presentations. To see the program and the list of all posters open <a href="http://www.cecp.at/index.php/cecp-archive">http://www.cecp.at/index.php/cecp-archive</a>

### Perspectives of Photochemistry in the New Millennium



After a break of six years, a new photochemistry meeting was announced. The name was quite complex: Austrian-German-Hungarian-Swiss Tetranational Symposium Perspectives of Photochemistry in the New Millennium organized mainly by Axel Griesbeck from Cologne with help from Thomas Bally from Fribourg, Günter Grampp from Graz, and Attila Horváth from Veszprém. As in 1998, the meeting was held in the Hotel Europäischer Hof in Bad Gastein. Again the lecture hall was rather crowded and the poster space was very limited. The program started on Sunday, March 7 with a lecture with experiments Playing with light - Thinking in excited states given by Michael Tausch from Duisburg. This was the beginning of the integration of chemical education in photochemistry into the scientific meetings in the Gastein valley. This tradition has been continued until nowadays. The meeting was again divided into a morning and evening session with a long break after lunch. One invited lecture has been presented by Peter Ogilby from Aarhus on The singlet oxygen microscope: From phase-separated polymers to single biological cell. Plenary lectures were given by Silvia Braslavsky from Mülheim, Claudia Wickleder from Cologne, Horst Kisch from Erlangen, Christian Bochet from Fribourg, Bernhard Lang from Geneva, and Jószef Nyitrai from Budapest. The rest of the oral presentations were performed as lectures of 30 min including discussion: Teodor Balaban, Alfred Holzwarth, László Biczók, Bernd Strehmel, András Dombi, Stephan Landgraf, Ottó Horvath, Claudia Minkowski, Ulrich Steiner, Attila Horváth, Juliane Grota, Ulrich Grummt, Dietrich Döpp, Jochen Mattay, Helmut Görner, Klaas Zachariasse, Gonzalo Angulo, and Victor Martinez-Junza. In total 26 oral presentations were given. During two afternoon sessions, 29 posters were presented. After a short morning session on Thursday, March 11 the meeting closed.

To see the program and the list of all posters open <a href="http://www.cecp.at/index.php/cecp-archive">http://www.cecp.at/index.php/cecp-archive</a>.

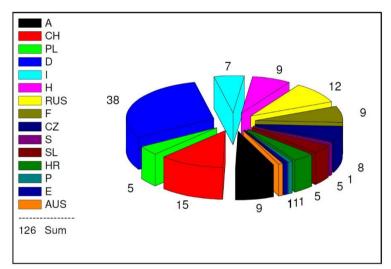
### Central European Conference on Photochemistry CECP

In 2006 a new format of the photochemistry meetings started. We moved to Bad Hofgastein only a few kilometers north of the former location. This village offered a brand new conference facility Kongress-Zentrum (congress center), which was built together with the Alpentherme (thermal bath & spa) in 2004. It is a multi-purpose location for different kinds of activities. For scientific conferences, the location can be divided into two halls, one for the lectures (up to 130 chairs) and one for poster presentation (up to 40 Posters), breaks, and dinners. A foyer is available as extra space (another 40 posters). Additionally, the location allows perfect access to physical activities during the afternoon break. Downhill and cross-country skiing, as well as winter walking-tours or the thermal bath and spa, offer a wide variety of possibilities to enjoy the region or to relax. Together with the scientific program, an ideal combination is present at this place.

The scientific organization has been done by the first international scientific committee: Axel Griesbeck from Cologne, Günter Grampp from Graz, Christian Bochet from Fribourg, Norbert Hoffmann from Reims, Nelsi Zaccheroni from Bologna, Attila Horváth from Veszprém, and Petr Klán from Brno. They suggested 13 possible candidates for an invited plenary lecture. The local organizer (Stephan Landgraf) collected applications for short talks (total 39). In an

evaluation process, the committee voted for the best lectures and talks. Following this list, the program was filled.

The key idea of the CECP meeting is to bring together young and experienced photochemists from all photochemical fields. Therefore, everything was done to enable scientist from all counties to join the meeting. Additionally, the evening should be undisturbed by the dinner. So four evening buffets were organized for all participants. The costs were included in the conference fee. Therefore, for students, the conference itself has been free of charge. Young researchers up to 4 years after PhD and all attendees from east European countries could join for a reduced fee, too. The success of this way to organize a conference could be seen in the number of countries present at CECP 2006 (Fig. 3).

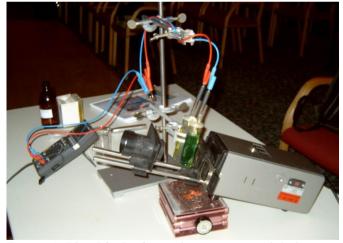


**Figure 3.** Registered attendees sorted by country. Finally, 121 participants arrived at Bad Hofgastein.

The main part of the income of CECP 2006 came from the fees of the participants. Additional funding could be obtained from the Czech Ministry of Education (via Petr Klán) and the Swiss Chemical Society (via Thomas Bally). Receipts (in cash and in-kind) from industry could also be achieved by the local organizer. Therefore, we could support 28 participants with a weaver of the registration fee

and partially with the cost of accommodation and travel. After 16 years of the drop of the iron curtain, this was an essential support for many participants from less favored regions to join the scientific community. This number gradually dropped down to 3 in 2020 due to the development in most of the countries in Europe. From the scientific point of view, Europe is united.

The conference started on Sunday, March 5, with the come together including a buffet and the special opening lecture of Dario Bassani from Bordeaux, Exciting supramolecular architectures. From Monday to Wednesday there were two sessions per day with one plenary lecture in each session (overall 7 plenary lectures), as well as 28 short talks, and three open- ended poster sessions in the evening (overall 86 poster presentations). Plenary lectures have been given by Horst Kisch from Erlangen, Wolfgang Kautek from Vienna, Nicola Armaroli from Bologna, Xavier Allonas from Mulhouse, Eric Vauthey from Geneva, and Luisa De Cola from Münster. A lecture with experiments was presented by Michael Tausch from Wuppertal under the title Effective Low-Cost Experiments for Teaching Photochemistry. So, we had a broad spectrum from basic education to recent scientific research.



**Figure 4.** *Photo Blue Bottle* experiments presented during experimental lecture [3].

As a result of this first organization, we found out that the number of posters should not be larger than 80. To see the program and the list of all posters open <a href="http://www.cecp.at/index.php/cecp-archive">http://www.cecp.at/index.php/cecp-archive</a>.

In 2008 we wanted to learn from some difficulties during the former conference two years ago. We rearranged the position of the poster boards, tried to get some more space for dinner, and shifted the schedule to February, as this is more compatible with semester breaks in many European countries (except Germany). Due to an increased advertisement, we could attract five companies to book a booth at the conference. Additional funding from DFG (German Science Foundation via Jochen Mattay) for invited speakers and German students was also gratefully acknowledged. These two additional fundings offered some flexibility for the support of some participants from less favored regions. In order to improve the organization, especially during registration, we installed a conference secretary (Christine Onitsch) responsible for a smooth workflow. Finally, 113 photochemists from 18 different countries came together to share their results and experiences at the Congress Center of Bad Hofgastein. The scientific organization has been done by the international scientific committee: Dario Bassani from Bordeaux, Günther Knör from Linz, Eric Vauthey from Geneva, Otto Horváth from Veszprém, Kamil Lang from Rez, Nikita Lukzen from Novosibirsk, Jochen Mattay from Bielefeld, and Luca Prodi from Bologna.

This time the conference started on Sunday, February 10, with the come together including a buffet and the special opening lecture of Dimitra Markovitsi from Paris, president of EPA, *Collective effects in the UV interaction with DNA helices.* She also gave some recent information about the EPA. The schedule of the conference was similar to 2006 except that we removed the coffee break during the afternoon sessions.

From Monday to Wednesday 6 plenary lectures, 27 short talks (including one experimental lecture), and 63 posters were presented. Plenary lectures have been given by Attila Horváth from Veszprém, Sven Rau from Jena, Alexey Baklanov from Novosibirsk, Jean-Pierre Desvergne from Bordeaux, and Salvatore Sortino from Catania.

To see the program and the list of all posters open <a href="http://www.cecp.at/index.php/cecp-archive">http://www.cecp.at/index.php/cecp-archive</a>.



**Figure 5.** Plenary speaker gallery of CECP 2008 (in order of their appearance).

Another innovation was that we tried to bring CECP and EPA closer together. During a discussion at the meeting, we decided that next time in 2010 we will ask for the membership during registration and offer a reduced fee (with reimbursement by EPA).

We founded an Austrian section of EPA with Stephan Landgraf as chairman and Günter Grampp as vice-chairman. A general meeting of EPA Austria was held at the CECP 2008 meeting. EPA Austria is organized as a local group of EPA. We collect the regular EPA fee and transfer it annually to EPA. There are no additional local fees. Activities in Austria are financed by sponsoring. Until today most members are from the Graz University of Technology.

To see the program and the list of all posters open <a href="http://www.cecp.at/index.php/cecp-archive">http://www.cecp.at/index.php/cecp-archive</a>.

CECP 2010 was held from Sunday, February 7 to Thursday, February 11 at the same place. Again the international scientific committee changed to Thorsten Bach from Munich, Uwe Pischel from Huelva, Silvio Canonica from Duebendorf, Elena Selli from Milano, László Biczók from Budapest, Xavier Allonas from Mulhouse, and Petr Slaviček from Prague. Sabine Richert (formerly Graz, today Freiburg) was upgraded as conference secretary, a position she holds until today.



Figure 6. Plenary speaker gallery of CECP 2010 (in order of their appearance).

Plenary lectures have been given by Julia Pérez-Prieto from Valencia on *Photoactive nanoparticles*, Stefan Hecht from Berlin on *Chemical approaches to nanoscience*, Esther Oliveros from Toulouse on *Photochemically enhanced Fenton reactions*, Eric Vauthey from Geneva on *Ultrafast photoinduced processes at liquid interfaces*, Fausto Elisei from Perugia on *Ultrafast time-resolved spectroscopic investigations*, and Keitaro Nakatani from Cachan on *Organic photochromic systems in the solid-state*. The experimental lecture on *Teaching Basics of Photochemistry: Instant Luminescent Experiments* of Michael Tausch from Wuppertal was presented together with Claudia Bohrmann-Linde and Simone Krees.

The program was completed with 28 short talks and 76 poster presentations. Additional funding from DFG (German Science Foundation via Thorsten Bach) for invited speakers was also gratefully acknowledged. For the first time, we could attract a speaker from the USA: Steffen Jokusch from New York.

In 2010 there was plenty of snow in Bad Hofgastein as shown in Fig. 7. To see the program and the list of all posters open <a href="http://www.cecp.at/index.php/cecp-archive">http://www.cecp.at/index.php/cecp-archive</a>.



Figure 7. Congress center of Bad Hofgastein. Photo from 2010.

In **2012** the international scientific committee was formed by Fred Brouwer from Amsterdam, Sebastiano Campagna from Messina, Ottó Horváth from Veszprém, Tomas Polivka from Ceske Budejovice, Jacques-E. Moser from Lausanne, Esther Oliveros from Toulouse, and Dominik Wöll from Konstanz.

We were very glad, that Franco Scandola from Ferrara, one of the organizers of the first Gastein meeting (GAIPHOS) came back to open the conference with a plenary lecture on *Supramolecular strategies towards functional units of artificial photosynthesis* on Sunday 5.



Figure 8. Plenary speaker gallery of CECP 2012 (in order of their appearance).

Further interesting lectures were given by Rienk van Grondelle from Amsterdam on Photosynthetic Light-Harvesting: Lessons From Nature, Mike Heilemann from Würzburg on Imaging cellular structures with near-molecular resolution using photoswitchable fluorophores, László Biczók from Budapest on Photochemistry and photophysics of alkaloids and their supramolecular complexes, Sylvie Lacombe from Pau, on Photocatalysis and photosensitization as green process for the treatment of VOCs and foul odours: from material chemistry to the detection of reactive species, and Frank Nüesch from Dübendorf on Electronic processes at organic optoelectronic device interfaces. The experimental lecture of Michael Tausch from Wuppertal was presented together with Simone Krees on Teaching Photochemistry - Photochromism and Photosteady State. 24 short talks and 74 poster presentations completed the program.

To see the program and the list of all posters open <a href="http://www.cecp.at/index.php/cecp-archive">http://www.cecp.at/index.php/cecp-archive</a>.

Two years later, in 2014, CECP was held from Sunday, February 9 to Thursday, February 13. The international scientific committee was formed by Mike Heilemann from Frankfurt, Bo Albinsson from Gothenburg, Dominik Heger from Brno, Christian Bochet from Fribourg, Luca Prodi from Bologna, and Christian Ley from Mulhouse.

A very hot topic was presented by Markus Sauer from Würzburg on Localization microscopy coming of age: From concepts to biological impact. In the same year, Stefan Hell (et al.) from Göttingen received the Nobel Prize for Chemistry for the development of super-resolution microscopy. This was a brilliant input for most researchers in the audience on these new methods in fluorescence.



Figure 9. Plenary speaker gallery of CECP 2014 (in order of their appearance).

More plenary lectures were given by Oliver Wenger from Basel on Proton-coupled electron transfer with photoexcited metal complexes, Joakim Andréasson from Gothenburg on Molecular photoswitches in logic and biological systems, Tomas Polívka from Ceske Budejovice on Carotenoid photophysics-rich excited-state properties of seemingly simple molecules, Fausto Puntoriero from Messina on Ultrafast energy dynamics in multiBODIPY supramolecular system, and Pascale Changenet-Barret from Gif-sur-Yvette on the Study of the intrinsic fluorescence properties of peculiar DNA structures and their interactions with ligands. 24 short talks and 63 posters were presented during the conference.

The scientific part closed with the experimental lecture from Michael Tausch and Claudia Bohrmann-Linde from Wuppertal, and Simone Krees from Münster on *Teaching Photochemistry - Experiments and Concepts*.

In contrast to the two former meetings, there was very little snow in 2014. Thanks to global warming. To see the program and the list of all posters open <a href="http://www.cecp.at/index.php/cecp-archive">http://www.cecp.at/index.php/cecp-archive</a>.



Figure 10. Congress centre of Bad Hofgastein. Photo from 2014.

In **2016** EPA Austria has become a registered association (ZVR: 050416508) in order to improve the financial management of CECP. The first elected chairman and vice-chairman are Stephan Landgraf and Günter Grampp both from Graz, respectively.

CECP 2016 was held from Sunday, February 14 to Thursday, February 18. A special week, associated with a local carnival tradition (Fasching) forced us to a later schedule. As all the meetings before we changed the members of the international scientific committee: Michael Tausch from Wuppertal, Andrzej Sobolewski from Warsaw, Petr Klán from Brno, Alexandre Fürstenberg from Geneva, Sylvie Lacombe from Pau, and Alberto Credi from Bologna.

The committee selected as plenary lectures: Stefan Hecht from Berlin on Photoswitches as key ingredients for remote spatio-temporal control, Paola Ceroni from Bologna on Light-harvesting antennae based on luminescent silicon nanocrystals, Jacek Waluk from Warsaw on Various ways of looking at single molecules, Suzanne Fery-Forgues from Toulouse on The Tao of solid-state fluorescent organic molecules: On the Way to luminescent microfibers and nanoparticles for biomedical imaging, Petr Slavicek from Prague on Computational Photodynamics: From UV to X-ray domain, and Natalie Banerji from Fribourg on The Photophysics behind Organic Electronics. Additionally, 24 short talks and 75 posters were presented.

For the first time the experimental lecture was not presented from someone from the Tausch group and former co-workers, but from Jennifer Dörschelln and Amitabh Banerji from Cologne on OLED OPV to Go.

As the XXVIth IUPAC International Symposium on Photochemistry was held in Osaka in 2016 EPA decided to use CECP as the platform for their General Assembly and the prize ceremony for the EPA PhD Prize of the Best PhD Thesis in Photochemistry for Tomas Slanina

from Brno and the EPA-PPS Prize for the most highly cited paper published in PPS during the previous two calendar years for Fausto Ortica from Perugia. Both prize winners got the opportunity the present their recent results in photochemistry. This part was closed by Alexandre Fürstenberg with a brief review of the activities of the International Year of Light in 2015.



Figure 11. Plenary speaker gallery of CECP 2016 (in order of their appearance).

We closed the meeting with the *Bauernbuffet* celebrating the 10<sup>th</sup> anniversary of CECP and the EPA General Assembly on Wednesday evening.

To see the program and the list of all posters open <a href="http://www.cecp.at/index.php/cecp-archive">http://www.cecp.at/index.php/cecp-archive</a>.



**Figure 12.** 10<sup>th</sup> anniversary logo with the flags of all countries with at least one chairman in the scientific committee.

From Sunday, February 4 to Thursday, February 8, 2018, 86 photochemists from 17 different countries came together to share their results and experiences at the Congress Centre of Bad Hofgastein. The scientific organization has been done by the international scientific committee: Mohamed Sarakha from Clermont-Ferrand, Dominik Heger from Brno, Heiko Ihmels from Siegen, Jacek Waluk from Warsaw, Oliver Wenger from Basel, Maurizio Fagnoni from Pavia, and as a guiding member: Stephan Landgraf from Graz for EPA Austria.



Figure 13. Plenary speaker gallery of CECP 2018 (in order of their appearance).

Plenary lectures have been given by Andreas Steffen from Würzburg on the Influence of metal-metal interactions on the excited states in d<sup>10</sup> coinage metal complexes, Martin Goez from Halle on Accessing the super-reductant eaq through sustainable photoionizations, Elena Selli from Milan on Photocatalytic materials: spectroscopic characterization in relation to photoactivity.

A new form of a discussion during a lecture - called *tandem lecture* - has been created by Gonzalo Angulo vs. Arnulf Rosspeintner (from Warsaw and Geneva, respectively) with the title *Flies On the Storm: a Dialogue About Diffusion In Photochemistry*. In this lecture, both presenters took a closer look at the diffusion, either of matter or of energy. It is very important to keep in mind that on the fast time-scale there is always a certain probability in a solution for a fast component without diffusion. Later many reactions are simply diffusion controlled. Sometimes recombination for two partners is necessary to overcome selection rules. This more complex description of (photo-)chemical kinetics has been explained in an understandable fashion.

Two more plenary lectures were given by Marcello Brigante from Aubière on *Photochemical generation of inorganic radicals: Environmental applications and polluted water remediation* and Radek Cibulka from Prague on *Flavins - not only cofactors but also efficient photocatalysts*.

The program was completed by 28 short talks (four held as tandem talks, two speakers from the same working group on a similar topic) and 41 posters. In 2018 CECP had less than 100 participants for the first time (see Tab. 2). We closed the meeting with the *Bauernbuffet* celebrating 20 years of photochemistry meetings in the Gastein valley.

The latest meeting till now was CECP 2020 held from February 9 to 13. 83 photochemists from 15 different countries came together to share their results and experiences. The scientific organization has been done by the international scientific committee: Jérôme Chauvin, Grenoble, F, Radek Cibulka from Prague, Maurizio D'Auria, President of EPA from Potenza, Tatu Kumpulainen from Geneva, Bernd Strehmel from Krefeld, and as a guiding member: Stephan Landgraf from Graz for EPA Austria. The conference started on Sunday with the get-together including a buffet and an opening lecture from Heinz Mustroph from Wolfen, on Cyanine Dyes - critical reviews of popular theoretical models for describing their electronic structure and

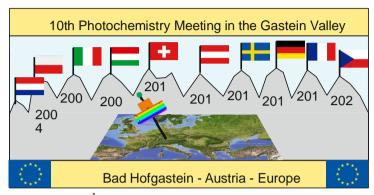
samples of photochemical hi-tech applications. Plenary lectures have been given by Yann Pellegrin from Nantes on Exploring new trends in the photochemistry of copper complexes(I)-bis(diimine), Filip Bureš from Pardubice on Organic push-pull molecules with tuneable properties: Towards dicyanopyrazine photoredox catalyst, Alberto Credi from Bologna on Light on molecular machines: from switches to motors, Arri Priimägi from Tampere on Azobenzene revisited: from light-driven robotics to optical humidity sensing, and an experimental lecture from Michael Tausch from Wuppertal on Towards artificial photosynthesis and molecular logics - experimental approaches in chemical education. 24 short talks (two held as tandem talks) and 46 poster presentations completed the schedule of the meeting. To see the program and the list of all posters open <a href="http://www.cecp.at/index.php/cecp-archive">http://www.cecp.at/index.php/cecp-archive</a>.



Figure 14. Plenary speaker gallery of CECP 2020 (in order of their appearance).

We closed the meeting with the *Bauernbuffet* celebrating the 10<sup>th</sup> photochemistry meeting in the Gastein valley.

CECP 2020 was not influenced by the new Coronavirus as the last international meeting on photochemistry worldwide. After this, all meetings have been canceled or held online.



**Figure 15.** 10<sup>th</sup> photochemistry meeting in the Gastein valley logo with the flags of all countries with at least one chairman in the scientific committee.

#### **CECP** awards

From the beginning of CECP in 2006 till now two young scientists have been honored the CECP award for the best talk and the CECP award for the best poster presentation at each CECP conference. As shown in Tab. 1 young researchers from different research groups have been chosen by the international scientific committee. Some of them are still active in the photochemistry community.

#### **CECP** organization

Local organizer of CECP 2006 to 2020: Stephan Landgraf, chairman of EPA Austria, all work before the meeting (applications, registrations, finance management, contact to the conference center, the book of abstracts, reports, supports, etc.), local coordinator at the meeting.

Members of the local organizing committee during the years (in order of their first appearance): Heidi Schmitt, Nararak Leesakul, Claudia Muresanu, Anne-Marie Kelterer, Dana Dvoranová, Christine Onitsch, Asim Mansha, Martin Knapp, Sabine Richert, Sadia Asim, Kraiwan Punyain, Truong Nguyen Xuan, Alexander Wankmüller, Anna-Maria Wernbacher, Sebastian Hanft, Agnieska Burczyk, and Jens Sobek.

#### **Appendix**

**Table 1:** CECP awards

Year	Award for best talk	Award for best poster
2006	David Bailey, Bremen	Katja Draxler, Konstanz
2008	Dominik Wöll, Konstanz	David Carteau, Bordeaux
2010	Simone Draxler, Munich	Sabine Richert, Graz
2012	David Bléger, Berlin	Franziska Graupner, Munich
2014	Fillipo Monti, Bologna	Jesper Nilson, Gothenburg
2016	Anne Fuhrmann, Berlin	Maria Pszona, Warsaw
2018	Julien Christmann, Mulh.	Goawa Naren, Gothenburg
2020	Matiss Reinfelds, Graz	Marina Russo, Brno

**Table 2**: Registered participants of GAIPHOS, PPNM, and CECP 2006 to 2020

						Sum
1998						85
2004						70
	RP	YR+EE	ST	AP	IND	
2006	39	34	52	7	1	133
2008	44	29	39	10	7	129
2010	42	20	53	9	4	126
2012	34	27	50	4	2	117
2014	38	19	49	3	3	112
2016	36	24	47	2	6	115
2018	33	22	31	3	6	95
2020	24	25	28	1	5	83

RP: regular participant, YR: young researcher with less than 4 years from PhD, EE: east European participant, ST: student without PhD, AP: accompanying person, IND: industry person.

**Table 3**: Sponsors of GAIPHOS, PPNM, and CECP 2006 to 2020 Public funding agencies:

Swiss Society of Photochemistry	2004, 2006, 2010
German Chemical Society	2004
German Science Foundation	2008 to 2014
Czech Ministry of Education	2006
EPA	2010 to 2020
Land Salzburg, local governor	2012

Private companies (in order of their first appearance):

VWR International GmbH 2006
EXCEL Techn. Europe GmbH 2008
TOPTICA Photonics AG 2008, 2018
HORIBA Jobin Yvon GmbH 2008, 2010
Quantel SA 2008 to 2016

 Ocean Insight (Ocean Optics)
 2008, 2010, 2018, 2020

 Radiant Dyes Laser Acc.
 2008, 2010, 2012

PicoQuant GmbH 2008 to 2020, except 2012

Coherent (Deutschland) GmbH 2008

Hamamatsu Deutschland GmbH 2010 to 2020

ID Quantique SA 2012
Shimadzu Österreich GmbH 2012
Edinburgh Instruments 2014, 2016
Gilden Photonics 2014
GWU-Lasertechnik 2014
NKT Photonics GmbH 2014

TOPAG Lasertechnik 2016 to 2020 Karl Brieden, Peschl Ultraviolet 2016, 2020 ESKPLA 2016 to 2020

Laser Quantum 2018 MDPI ("Catalyst") 2020

Local companies:

Steiermärkische Sparkasse, Graz 2008 to 2020 Raiffeisenbank, Graz 2008

#### References

- 1. Private photo send by Horst Kisch.
- 2. Scan from the book of abstracts cover page.
- 3. Photo taken by Heidi Schmitt after the presentation on 2006-03-08.



See you again ...

## ABSTRACT OF THESIS ON PHOTOCHEMISTRY

## Photochemical decarboxylation of phthalimide derivatives

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Photodecarboxylation has been intensively investigated, regarding its importance in organic synthesis¹ and the fact that some nonstereoidal antiinflamatory drugs undergo photodecarboxylation, causing severe side effects.² Photoinduced electron transfer (PET)-promoted decarboxylation, with phthalimide in the triplet excited state as an oxidizing agent, has been used in the synthesis of macrocyclic compounds³ and cyclic peptides.⁴ Furthermore, PET-promoted decarboxylation gives free radicals that can be trapped with different electron-deficient alkenes and give addition products.⁵

First part of the PhD thesis involved a study of the influence of distance between the electron acceptor (phthalimide) and the electron donor (carboxylate) linked via adamantane moiety on the PET and photodecarboxylation efficiency. Therefore, nonsubstituted phthalimide derivatives 1-5 were synthesized (Figure 1) and their photochemical reactivity investigated. To probe for the reactivity of triplet excited states which are anticipated to be involved in the PET and decarboxylation, laser flash photolysis was performed. Apart from ubiquitous "simple" decarboxylation (-COOH  $\rightarrow$  -H) for 1-5, the photoreactions of 2 and 3 afforded more complex polycyclic molecules 2P and 3P, respectively (Figure 1).6 Furthermore, quantum yields of the photodecarboxylation reaction depend on the distance between the donor and acceptor,6 but the measured lifetimes of the triplet excited state did not provide the rates of PET.<sup>7</sup>

Investigation of the photochemical reactivity of **4** in  $\beta$ -cyclodextrin ( $\beta$ -CD) revealed that  $\beta$ -CD does not affect the decarboxylation efficiency, but has an influence on the subsequent photochemical H-

abstraction. Irradiation of 4 in the presence of acrylonitrile within  $\beta$ -CD leads to decarboxylation and formation of the corresponding azomethine ylide **4AY** (Figure 1), which was trapped by acrylonitrile in a [3+2] cycloaddition.<sup>8</sup>

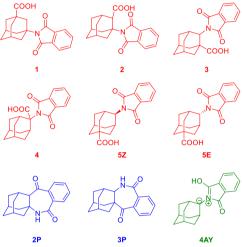


Figure 1. Nonsubstituted phthalimide derivatives 1-5 (red), photoproducts 2P and 3P (blue) and azomethine ylide 4AY (green).

The second part of the PhD thesis was focused on the study of substituent effects on the phthalimide on the photochemical reactivity and photophysical properties. Therefore, substituted phthalimide derivatives 6-10 (Figure 2) were synthesized and their reactivity was investigated by preparative irradiation, fluorescence spectroscopy and laser flash photolysis (LFP). The photophysical properties and the reactivity in decarboxylation were put in connection with the estimated  $pK_a$  values of the corresponding functional groups on the phthalimide.

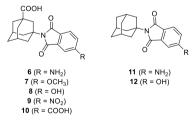


Figure 2. Substituted phthalimide derivatives 6-12.

Phthalimides **6-8** are fluorescent ( $\Phi_F = 0.02\text{-}0.66$ ) and react in the PET and decarboxylation *via* singlet and triplet excited states. Triplet excited states and the corresponding phthalimide radical anions formed in the PET were detected in aqueous solutions by LFP, but the rate constants for PET could not be revealed.<sup>9</sup>

Substitution of the phthalimide by amino group gives rise to photochemically stable compounds that are characterized by a charge transfer (CT) character of the excited state and solvatochromic properties. Thus, adamantyl derivative 11 (Figure 2), which is amphiphilic, can be applied for fluorescence microscopy as a solvatochromic dye in selective visualization of lipid droplets and mitochondria. 10

Antiproliferative and antiviral testing against tumor cells and viruses were conducted for a set of different adamantylphthalimides. For **11** and **12** (Figure 2), antiproliferative activity against H460, MCF-7, MOLT-4 and A2780 tumor cell lines was in micromolar range and minor antiviral activity against cytomegalovirus and varicella-zoster virus was found.<sup>11</sup>

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## Diversity of the Photosensitization Mechanisms of Surface-functionalized Oxide Semiconductors

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Modern heterogeneous photocatalysis involves many methods to modify semiconductors in order to improve their physicochemical properties. However, some problems associated with their usage still require solutions. The goal of this dissertation was to verify several research hypotheses related to photosensitization of surface-functionalized oxide semiconductors.

One of the methods used to modify titanium(IV) oxide is sensitization with organic compounds that can form a charge-transfer complexes on its surface. Such materials exhibit high photoactivity in the visible light range, but most of them rapidly degrade as a result of reactions with photogenerated reactive oxygen species. It happens due to the oxidation of the aromatic ring by photogenerated hydroxyl radicals, however it can result in formation of hydroxylated derivatives which have ability to bind to titanium(IV) oxide to form new charge-transfer complexes that can also absorb visible light. Despite the degradation of the starting modifier, compounds appeared in the system can photosensitize TiO<sub>2</sub> and prolong its activity. As the

reaction progresses, these complexes completely degrade and after some time they decompose into simple inorganic molecules. It is not a permanent effect, but it can noticeably improve the photoactivity of such a photocatalyst, despite overall low stability of systems: organic molecue-TiO2. The solution to the problem of photostability of organic photosensitizers in such system could be their protection against the mentioned reactive oxygen species, e.g. by covering them with a thin layer of the same semiconductor. Under an appropriately thin TiO<sub>2</sub> layer, the photosensitizer should retain its photocatalytic properties, while gaining protection against reactive oxygen species. To verify this hypothesis, a series of materials based on pure nanocrystalline anatase and a mixture of nanocrystalline anatase and rutile in a ratio of 78:14, sensitized with catechol, 2,3-naphthalenediol, 2,5-dihydroxyterephthalic acid and hexachloroplatinic(IV) acid (Fig. 1) and modified with small amount of TiO<sub>2</sub> deposited by atomic layer deposition (ALD) were tested.

The measurements showed that the deposition of titanium dioxide with ALD does not cause noticeable changes in spectroscopic properties for most of the materials. The observed differences were subtle, without a visible trend, which could indicate a non-

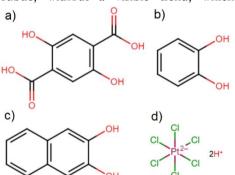


Figure 1. Structures of used modifiers:
a) 2,5-dihydroxyterephthalic acid,
b) catechol, c) 2,3-naphtalenodiol,

d) chloroplatinic(IV) acid.

homogeneous deposition of TiO<sub>2</sub> at the surface of tested photocatalysts. Only the samples modified with 2,5-

dihydroxyterephthalic acid showed a trend associated with increase in intensity within the complex band maximum with increase in the amount of deposited TiO<sub>2</sub>. This behavior was probably caused by binding of added titanium(IV) oxide

to the free -COOH and -OH groups of the photosensitizer. Modification with hexachloroplatinic(IV) acid resulted in self-degradation to metallic platinum (gray color change) in the case of a mixture of anatase and rutile, whereas for pure anatase the formation

of a new surface complex between platinum and titanium dioxide,<sup>3</sup> absorbing visible light, was observed. A part of materials modified by ALD improved their photoelectrochemical properties, while others ceased to exhibit photoelectrochemical activity in the visible light range. Photoactivity measurements showed a general trend for all materials, indicating a decrease in hydroxyl radical generation efficiency with an increase in the amount of TiO<sub>2</sub> deposited by ALD. Probably the deposition of additional titanium(IV) oxide at the surface of the photocatalyst limits access to surface complexes for both reactive oxygen species and other reagents. Most of the materials worsened their photostability as a result of modification with ALD, but some of them obtained the required parameters. Performed measurements showed that the greater amount of TiO2 deposited by ALD method for some samples will probably improve their photostability, therefore these materials have been patented ("Wielowarstwowy fotokatalizator aktywowany światłem widzialnym i sposób jego otrzymywania" 2013, nr UPRP: P. 406 707). It seems that accurate control of the described process due to the uneven deposition of additional TiO<sub>2</sub> at the surface of powder materials is very difficult. However, this is a kind of strategy to protect photocatalysts against degradation as a result of exposure to photogenerated reactive oxygen species, although it is associated with a decrease in photoactivity.

Improvement of photostability of titanium(IV) oxides modified with organic compounds can also be achieved by using chromophores, which are more resistant to reactive oxygen species. Organic dyes derived from 9,10-anthraquinone have been known for millennia as permanent pigments used in the production of ceramics or clothing. A para-quinone system is present in their structure, which is known from reducing properties, moreover 9,10-anthraquinone itself is known for its resistance to oxidation, even with such drastic reagents as hot chromic acid.<sup>4</sup>

The hydroxy anthraquinone derivatives bind very well to the surface of titanium(IV) oxide due to the presence of –OH groups, so that the 1,2-dihydroxyanthraquinone-TiO<sub>2</sub> system is often used as a model in quantum chemical calculations. Dihydroxyanthraquinone derivatives should exhibit greater photostability than systems with catechol, and due to the possibility of sensitization of TiO<sub>2</sub> they should enable synthesis of efficient photocatalysts. To verify this hypothesis, photocatalysts based on TiO<sub>2</sub> (nanocrystalline anatase and a mixture

of nanocrystalline anatase and rutile in a ratio of 78:14) modified with 1,2-dihydroxyanthraquinone, 1,4-dihydroxyanthraquinone, 1,5-dihydroxyanthraquinone (Fig. 2) were synthesized and tested.

The conducted research showed that photocatalysts based on dihydroxy derivatives of anthraquinone and titanium(IV) oxide are efficient and durable. Each of the described organic compounds

**Figure 2.** Structures of used modifiers:

- a)1,2-dihydroxyantraquinone,
- b)1,4-dihydroxyantraquinone,
- c)1,5-dihydroxyantraquinone,
- d)1,8-dihydroxyantraquinone.

bound to TiO2 in a different way, which was inferred from previously published calculations and performed adsorption tests. Dihydroxyanthraquinone derivatives binding to TiO<sub>2</sub> excite it by the photoinduced electron transfer (PET) mechanism,5 which was confirmed bv measurements of the incident photon to photocurrent efficiency (IPCE) and action spectra. The

IPCE values were recorded for the area of bare TiO2 activity, while they were smaller for the visible light range. This photoelectroactivity separation comes from the weak binding in the TiO2-photosensitizer system, which leads to the PET mechanism. In the photodegradation reaction of 4-chlorophenol lasting 180 minutes, the most active material was catechol@anatase. However, during a long lasting tests of acid photooxidation terephthalic (300 min), a part of dihydroxyanthraquinone-based materials were more active, which is due to their greater durability. This was also confirmed in solid state photostability tests, where the degradation constant determined for the 1,5-dihydroxyanthraquinone@anatase material was several orders of magnitude smaller than for the other tested materials. The measurements confirmed the research hypothesis that the dihydroxy derivatives of anthraquinone due to the possibility of sensitization of TiO<sub>2</sub> should be more efficient photocatalysts, and also have greater photostability than known catechol-based systems.

Studies on photocatalyst activity often aim at determining the influence of used modification method on the course of photocatalytic processes. Usually the type of used modifier, the effect of temperature on the type of crystalline phase obtained or the size of deposited noble metal nanoparticles are considered as the most important factors. Seemingly insignificant factors such as the type of used reducer, the intensity of the sample abrasion in the mortar or the effect of the solvent on the population of water molecules at the surface of the semiconductor are very rarely taken into account. These less "drastic" operations can realistically moderate the photocatalytic properties of the used materials. To verify this hypothesis, the properties of titanium(IV) oxide, modified by deposition of small amounts of TiO<sub>2</sub> at its surface using ALD method were examined, and then the impact of these modifications on visible light activity was determined.

The conducted tests showed that the deposition of small amounts of TiO2 does not affect the size of crystallites or phase composition of the tested photocatalysts. Also, measurements with the scanning electron microscope did not reveal any morphological differences between unmodified samples and those even after 10 nm of TiO<sub>2</sub> deposition. Only negligible differences were observed for some of the samples in specific surface area, UV-vis spectra and catechol adsorption at the surface of a given photocatalyst. Measurements of the density of electronic states and photocurrent generation revealed greater differences between the tested materials. A significant effect on each of these parameters was observed, but without a clear trend. The photocatalytic activity of the tested materials was also different. The efficiency of hydrogen generation as well as photoxidation of terephthalic acid during irradiation with ultraviolet light was different for each of the materials, however the largest changes were recorded for measurements in the visible light range. For both applied titanium(IV) oxides (nanocrystalline anatase and a mixture of nanocrystalline anatase and rutile in a ratio of 78:14), samples modified with 0.5 nm TiO<sub>2</sub> applied with ALD showed two or even three times better photogeneration efficiency of hydroxy terephthalic acid. The obtained results encouraged the author to further research on seemingly insignificant effects affecting photocatalytic properties. As part of cooperation, the impact of synthetic procedures used during gold deposition on semiconductor surfaces was examined. The

conducted experiments showed that in some cases (materials obtained by photodeposition), the use of just reducing agents without a gold precursor, can change the properties of a given material to a greater extent than gold nanoparticles deposited at the surface.

Subtle modifications, which include the deposition of small amounts of TiO<sub>2</sub> at the surface of titanium(IV) oxide by ALD method can noticeably affect visible photoactivity by changing the distribution and density of TiO<sub>2</sub> electronic states. These subtle modifications also include mild reducing and oxidizing agents, which in some cases appear to have a greater effect on the photocatalytic properties of the material than the modifier itself.<sup>6</sup>

The last part of the research described in referred thesis concerned the second most popular broadband semiconductor used in photocatalysis - zinc oxide. Many researchers point to this semiconductor as more efficient in some applications than titanium(IV) oxide. Because ZnO is difficult to photosensitize to visible light using organic compounds, its comparison with TiO2 was performed on materials obtained by gold photodeposition. In the case of deposition of noble metals at the surface of semiconductors, a localized surface plasmon can be considered. It can interact with semiconductors through three mechanisms: light scattering/trapping, plasmon-induced resonance energy transfer or hot electron injection. While the first mechanism concerns high energy radiation, the other two may be responsible for photosensitization to visible light. To determine which of them is responsible for photosensitization of ZnO with Au nanoparticles, a series of photocatalysts based on various ZnO materials containing different amounts of gold on their surface was obtained and tested.7

It was found during the tests that as the amount of deposited Au was increasing, a larger nanoparticles were obtained and their agglomerates were growing. In addition, only some of the materials had a band with a clear maximum without any broadening towards longer wavelengths coming from the plasmon. All zinc oxide based materials obtained by gold photodeposition showed greater photocatalytic activity than the reference material based on titanium(IV) oxide in the process of photoxidation of isopropanol to acetone in the visible light range. The most active samples were 8 to 10 times more active than TiO<sub>2</sub>-based material. The analysis of emission spectra showed that in the case of the tested materials ZnO photosensitization probably occurs through the mechanism of hot

electron injection. Conducted research can be considered as a preliminary tests and certain confirmation of the mechanism responsible for visible light photosensitization requires further tests, which are in further plans.

A list of publications arising from the thesis:

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#### Acknowledgment:

Ideas Plus (MNiSW) 0003/ID3/2012/62, Opus 10 (NCN) 2015/19/B/ST5/00950

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#### Preparation of Quinone Methides and Investigation of their Biological Effects

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This thesis describes multi-step synthesis of two quinone methides (QM) precursor classes. Photochemical reactivity and photophysical properties of prepared QM precursors 1-5 were investigated by photosolvolysis and spectroscopic techniques — UV-vis and fluorescence spectroscopy and laser flash photolysis (LFP).

**Figure 1.** Structure of homobifunctional quinone methide (QM) precursors 1-3 and heterobifunctional precursors 4 and 5.

First class - homobifunctional QM precursors 1-3 contain two equal QM precursors; phenol, naphthol or anthrol subunits, linked by a flexible alkyl chain. Generation of QMs in the phenol subseries 1 was achieved by fluoride addition and the formation of QM was indirectly proved by the isolation of azide and methanol adduct. Unfortunately, expected cross-linking of DNA strands has not been confirmed and the compounds do not possess antiproliferative activity which was explained by the impossibility to form bifunctional QMs.<sup>1</sup>

Generation of QM in the naphthol 2 and anthrol 3 subseries was achieved in a photochemical dehydration reaction. QMs were detected by LFP and were also indirectly confirmed by the isolation of methanolysis photoproducts. Methanolysis of naphthol derivatives 2 taking place via photodehydration is in competition with symmetry breaking charge separation (SB-CS). The SB-CS gave rise to radical ions 2-RIP that were also detected by LFP. In the aqueous solvent,

excited state proton transfer (ESPT) competes with the abovementioned processes, giving naphtholates  $20^-$  (Scheme 1), but the process is inefficient and can only be observed in the buffered aqueous solution at pH  $> 7.2^-$ 

Scheme 1. Plausible photochemical pathways for bisnaphthols 2.2

Biological activity of naphthol 2 and anthrol 3 subseries was investigated by alkaline agarose gel electrophoresis and MTT tests on human cancer cell lines. Alkaline agarose gel electrophoresis did not show the possibility of cross-linking DNA strands by QM generated from naphthol compounds 2. However, increased antiproliferative activity upon irradiation of cancer cell lines has been demonstrated, which may be associated with the QM formation. In the anthrol subseries 3 compounds shown antiproliferative activity without irradiation, but the cytotoxicity increased 10 - 100 times upon the irradiation. It remained unclear whether the activity of the anthrol compounds 3 can be attributed to the action of QMs only, or some other reactive intermediates and photoproducts are responsible for the antiproliferative activity. Since the alkaline agarose gel electrophoresis did not show the possibility to cross-linking DNA strands, enhanced antiproliferative activity is most likely associated with the alkylation of proteins present in the cell cytoplasm, as evidenced by photoinduced alkylation of bovine and human serum albumins.2

Second class - heterobifunctional compounds **4** and **5** contain a naphthol moiety as a QM precursor and a 1,8-naphthalimide as a DNA binding unit. Subunits are linked by a flexible alkyl chain.

Upon excitation of heterobifunctional compounds 4 and 5 nonradiative energy transfer (FRET) takes place from naphthol to the naphthalimide moiety, reducing the reactivity in QM formation. Furthermore, in compounds 4 photoinduced electron transfer (PET) occurs after naphthalimide excitation with the formation of naphthol radical cation and naphthalimide radical anion detected by LFP. A PET

mechanism can ultimately lead to the QM formation, but the process is inefficient.

Biological activity of heterobifunctional compounds 4 and 5 was investigated on human cancer cell lines. Despite the reduced possibility of photoinduced QMs generation, the studied compounds exhibit enhanced cytotoxicity upon irradiation on human cancer cell lines. Subseries 5 is particularly interesting since these compounds are not toxic without irradiation, whereas irradiation significantly increased the antiproliferative activity. Furthermore, compounds from subseries 5 show selective cytotoxic to the lung cancer cell line (H460).<sup>3</sup>

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#### Hybrid Inorganic Semiconductor Nanostructures for Solar Fuel Formation and Chemicals Production

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Supervisor of the PhD thesis: Prof. Giacomo Bergamini<sup>1</sup>

#### Introduction

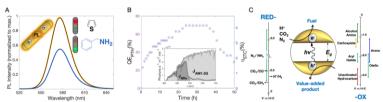
The work carried out in PhD work aims to capitalise on the most recent developments in the field of photo-redox catalysis to boost the sluggish reaction kinetics that hampers water-splitting. In the first place, oxidative organic transformation have been considered as alternative attractive routes to simultaneously generate two high-value added products, namely H<sub>2</sub> and small molecules of industrial

importance. Notably, the research was limited to mild and scalable reactions conditions, avoiding the use of high temperature and toxic solvents.

Later, this strategy has embraced a more extended gallery of redox reactions, i.e. CO<sub>2</sub> reduction, polymers photo-reforming, photo-polymerisations and hydrogenations. Having identified the most promising applications, but also the crucial limiting steps for each set of reactions, the knowledge acquired for batch processing has been extended to flow-microreactors. By chemical anchoring of the colloidal photocatalyst to microfluidic chips channels' surfaces, reaction performances are expected to benefit from improved mass transport, continuous replenishment of reagents and simultaneous removal of products, faster kinetics and finally ease of scale-up and scale-out from lab-devices to industrial systems.

#### Results

Figure 1A-C present the most relevant results obtained in the thesis, that focused on the investigation dot-in-rod CdSe@CdS system, a hybrid inorganic semiconductor nanostructure. In particular, Figure A shows the relevance of photoluminescence quenching as a ready-available, fast and cheap screening technique. This method has been applied to colloidal semiconductors for the first time, aiming at screening alternative oxidative half-reactions beyond water oxidation. Investigation of selected simultaneous decoupled photosynthetic red-



**Figure 1. A)** Fluorescence quenching method, a screening technique first applied to colloidal semiconductors to discover new oxidative reactions to be coupled to fuels production. **B)** Solar-driven photosynthetic production of hydrogen and benzaldehyde, with excellent photon-to-hydrogen quantum efficiency (QE<sub>PTH</sub>) and solar-to-chemical energy conversion efficiency ( $\eta_{STC}$ ). **C)** Schematic representation of the decoupled red-ox solar-to-chemical strategy using photosynthetic semiconductor systems.

ox reaction, we demonstrated a world-record efficiency in solar-to-chemical (STC) energy conversion. Remarkably, hydrogen and the industrially relevant benzaldehyde were produced with an STC efficiency of 4.2%, extremely close to the 5% threshold requested for market-penetration of this technology<sup>1,2</sup>. Moreover, with the newly proposed STC efficiency index, we effectively opened a new research line that aims at an extensive utilisation of solar radiation, through the simultaneous production of solar fuels (hydrogen, methane, ammonia..) and value-added chemicals, as schematised in Figure 1C<sup>3</sup>.

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#### CONFERENCE REPORT



#### **CECP 2020 Conference Report**

#### Stephan Landgraf, EPA Austria

From Sunday, February 9 to Thursday, February 13, 2020, 83 photochemists from 15 different countries came together to share their results and experiences at the Congress Centre of Bad

Hofgastein/Austria. It was a wonderful atmosphere and all participants enjoyed the meeting. The scientific organization has been done by the international scientific committee: Jérôme **Chauvin**, Grenoble, F, Radek **Cibulka**, Prague, CZ, Maurizio **D'Auria**, Potenza, I, Tatu **Kumpulainen**, Geneva, CH, Bernd **Strehmel**, Krefeld, D, and as a guiding member: Stephan **Landgraf**, Graz/A for EPA Austria (ZVR: 050416508). The conference started on Sunday with the gettogether including a buffet and an opening lecture.



**Fig. 1**: Yann **Pellegrin**, Nantes, F, Filip **Bureš**, Pardubice, CZ (first row), Alberto **Credi**, Bologna, I, Arri **Priimägi**, Tampere, FI, Michael **Tausch**, Wuppertal, D (second row).

From Monday to Wednesday there were two sessions per day with one plenary lecture in each session (5 plenary lectures and an experimental lecture of Michael **Tausch**, Wuppertal, D), as well as short talks (29 oral presentations), and a poster session every evening (46 poster presentations). Plenary lectures have been given by Filip **Bureš**, Pardubice, CZ, "Organic push-pull molecules with tunable properties: Towards dicyanopyrazine photoredox catalyst", Alberto **Credi**, Bologna, I, "Light on molecular machines: from switches to motors", Heinz **Mustroph**, Wolfen, D, "Cyanine Dyes – critical reviews of popular theoretical models for describing their electronic structure and

samples of photochemical hi-tech applications", Yann **Pellegrin**, Nantes, F, "Exploring new trends in the photochemistry of copper complexes(I)-bis(diimine)", Arri **Priimägi**, Tampere, FI, "Azobenzene revisited: from light-driven robotics to optical humidity sensing".

To keep the scientific level of the meeting on an internationally high one the scientific committee selected 5 plenary lectures and 29 (out of 34 applications) short talks. Four of these short talks have been presented as tandem talks with two presenters from the same working group. One additional talk on activities of EPA has been presented on Wednesday morning. All poster applications were accepted after checking by the local committee.

The local organizing committee has been formed by: Stephan Landgraf (local organizer from EPA Austria) and Sabine Richert. Additional help from Heidi Schmitt (also for the conference photos) is also gratefully acknowledged. The variety of different accommodations is available in Bad Hofgastein from private rooms up to hotels with high comfort. A contingent of 55 rooms (single and double) had been available for early booking until December 15. This year nearly all accommodations were booked out before the meeting started. Contact person for accommodation: Carina Schönegger, tourist office. Official web site of the meeting: <a href="https://www.cecp.at">www.cecp.at</a>

The key idea of the CECP meeting is to bring together young and experienced photochemists from all photochemical fields. Therefore, everything was done to remove all hindrance to join the meeting. Additionally the evening should be undisturbed by the dinner. So four evening buffets were organized for all participants. The costs were included in the conference fee. So, for students the conference itself has been free of charge. Young researchers up to 4 years after PhD, all attendees from Eastern European countries, and retired researchers could join for a reduced fee, too. A reduced fee for EPA members has been offered (30 € for full members and 15 € for students). For **CECP 2022** held in February 2022, in Bad Hofgastein a small increase of the fees has to be accepted to compensate inflation.

The location of the Conference Centre of Bad Hofgastein allows perfect access to physical activities during the afternoon break. Downhill and cross-country skiing, as well as the thermal bath and spa, offer a variety of possibilities to enjoy the region or to relax.

Together with the scientific program, an ideal combination is present at this place.



Fig. 2: Participants of CECP 2020 located on a Europe map.

Finally, 92 persons registered for the meeting until the beginning of the conference. Since 2006 there have been some fluctuations in the distribution of participants with a mean value of slightly above 100. Most of the participants come from Germany, but there was also significant attendance from France, Poland, Italy, Hungary, and the Czech Republic (with 5 participants and more).

The meeting is organized on a non-profit base. All travel grant applications have been accepted by the local organizer. 2 attendees (students) have been supported by this procedure. Statistics: RUS: 2.

#### CECP 2020 Awards for Young Scientists

There are two prices for young scientists to encourage them to present their best results at the CECP meeting. All oral and poster presentations have been evaluated by the international scientific committee. Both prices have been awarded at the end of the meeting at the closing ceremony.

CECP 2020 Award for best oral presentation: O18 Matiss **Reinfelds**, Graz, A "Rylene dyes as acceptors in organic solar cells"

The prize (valuable headset) was sponsored by TOPAG/EKSPLA.

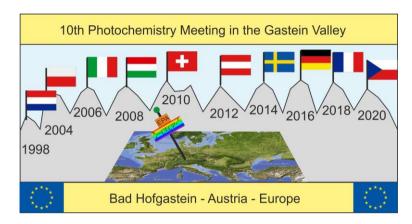


CECP 2020 Award for best poster presentation: P18 Marina **Russo**, Brno, CZ "Mechanisms of orthogonal photo-decarbonylation reactions of 3-hydroxyflavonebased acid-base forms"

The prize (200 € grant) was sponsored by MDPI/catalyst



Last but not least we celebrated the "10th Photochemistry meeting in the Gastein valley" with our "Bauernbuffet" on Wednesday evening.



**Tab. 1**: Former **CECP** awards:

Year	Award for best oral presentation	Award for best poster presentation
2006	David <b>Bailey</b> , Bremen/D	Katja <b>Draxler</b> , Konstanz/D
2008	Dominik <b>Wöll</b> , Konstanz/D	David <b>Carteau</b> , Bordeaux/F
2010	Simone <b>Draxler</b> , Munich/D	Sabine <b>Richert</b> , Graz/A
2012	David <b>Bléger</b> , Berlin/D	Franziska <b>Graupner</b> , Munich,D
2014	Fillipo <b>Monti</b> , Bologna/I	Jesper <b>Nilson</b> , Göteborg/S
2016	Anne <b>Fuhrmann</b> , Berlin/D	Maria <b>Pszona</b> , Warsaw/PL
2018	Julien <b>Christmann</b> , Mulhouse/F	Goawa <b>Naren</b> , Göteborg/S

## Conference Report on the SCS Photochemistry Section Symposium, June 19, 2020 (online)

Tatu Kumpulainen Department of Physical Chemistry, Sciences II, University of Geneva, 1211 Geneva 4, Switzerland

In response to the global pandemic causing world-wide travel restrictions, the SCS Photochemistry Section decided to organize its annual symposium online. The conference could be attended free of charge without geographical restrictions. This opened up many boarders and resulted in a record-high number of registered participants from 24 different countries. Most of the participants were from Switzerland followed by Germany and the United Kingdom. On the day of the event, over 90 participants gathered behind their screens to hear about the latest findings in photochemistry research in Switzerland and abroad. The organizing committee, consisting of the board of the Photochemistry Section, had selected a scientific program including 3 invited lectures, 4 short talks and 10 elevator talks that replaced the poster session. In addition, the general assembly of the Section was held online after the symposium.

The morning started with opening remarks from the Photochemistry Section President and conference chair, *Prof. Olivier Nicolet*. During his remarks, Olivier emphasized the importance of financial support from the sponsors, the Swiss Chemical Society (SCS), the European Photochemistry Association (EPA), Quantum Design Europe, and Helvetica Chimica Acta. This was followed by a brief introduction to the activities of EPA by one of their board members, *Dr. Alexandre Fürstenberg*:

The first session, chaired by *Dr. Tatu Kumpulainen*, begun with an invited lecture by *Prof. Peter Vöhringer* from the University of Bonn, Germany. Peter started with a topical introduction to global warming focusing on the staggering amount of CO<sub>2</sub> emissions from air travel. This highlighted the potential role of online conferences in reducing unnecessary greenhouse gas emissions. After the introduction, Peter gave an overview of different binding modes of a

CO<sub>2</sub> ligand on iron complexes and elucidated the full photochemical reaction cycle of ferrioxalate by time-resolved UV/IR spectroscopy. Ironically, excitation of ferrioxalate results in release of CO<sub>2</sub>, directly observed in the time domain for the first time, but Peter emphasized that his research may reveal novel ways for CO2 activation and hence its capture from the atmosphere. Peter's lecture was followed by two short talks. First, *Dr. Sara Cembellin* from the Autonomous University of Madrid, Spain, presented her work on the metal free, visible-light promoted synthesis of isothiazoles. Sara demonstrated the applicability of the approach on a large scope of substrates and discussed the detailed reaction mechanism. The session was concluded by Dr. Yinyin Bao from ETH Zurich, Switzerland, who demonstrated how the emission color of a single molecular fluorophore can be tuned in polymers. With a combination of experiments and multiscale modeling, he showed that the color tunability originates from through-space charge-transfer processes between the monomeric fluorophore and the polymer side chains or end groups.

The second session, chaired by Dr. Silvio Canonica, was started with an invited lecture by Prof. Kristopher McNeill from ETH Zurich, Switzerland. First, Kris gave a brief introduction to the role of triplet states in the photochemistry of chromophoric dissolved organic matter (CDOM). He further showed how a combination of laser spectroscopy and molecular probes can be used to obtain detailed mechanistic understanding on aquatic photochemistry. The main challenge arises from the complex and poorly defined mixture of chromophores present in the natural water samples. Therefore, comparative experiments with well-defined molecular probes are of key importance. During the discussion, it was funnily pointed out that most surface waters in Switzerland are poorly suited for his research due to the rather low CDOM content. Despite this, Kris continues his research in Zurich. Kris's lecture was followed by 10 elevator talks that replaced the poster session. During these 3 minute talks, the audience was introduced to various topics from thermally-activated delayed fluorescence to photosensitizers for various applications. Last talk of the session was given by Julien Dumouchel representing Quantum Design Europe. Julien gave a brief overview of their company and outlined the latest developments in Andor cameras for time-resolved applications.

The last session, chaired by **Prof. Oliver Wenger**, started with an invited lecture by Prof. Luisa De Cola from the University of Strasbourg, France. After a brief introduction to photophysics of Ptcomplexes, Luisa explained how to take advantage of molecular interactions to switch on the emission of these complexes. With the careful control of substituents and solvent properties, aggregates with different shapes (dots, rods and stars) and emission properties could be prepared. She then answered the puzzling question of how many Pt-units are required for aggregation-induced emission. Spoiler alert, the answer is three. She also demonstrated how the Pt-aggregates can be coated with capsid proteins to achieve virus-like nanoparticles with enhanced emission properties. Last, she showed her latest results on a 3D-imaging platform based on hydrogels labeled with luminescent Iridium-complexes. The last session featured also two short talks. **Prof. Paul Elliot** from the University of Huddersfield, UK, presented his detailed studies on unravelling the photophysics of Iridium-based luminescent complexes. He demonstrated how the relative energies of the excited states can be tuned by chemical modification of the ligands to achieve dual emission. Last, Dr. Bogdan Dereka from the University of Chicago, USA, discussed his findings on solvent tuning of photochemistry upon excited-state symmetry breaking in quadrupolar and octupolar compounds. He demonstrated that symmetry breaking in polar solvents is fast and results in strong enhancement of the photochemical reactivity.

Before the closing remarks, the managing editor of Helvetica Chimica Acta, *Dr. Richard Smith*, awarded the prizes for the best



**Figure 1.** Winners of the Helvetica Best Presentation Awards: (left to right) Sara Cembellin, João Avó and Steffy Becht.

short talk and two elevator talks sponsored by the same journal. The organizers wish to congratulate *Dr. Sara Cembellin*, the Autonomous University of Madrid, for the best short talk and *Dr. João Avó*, the University of Lisbon, and *Dr. Steffy Becht*, the University of Heidelberg, for the best elevator talks.

Following the success of the events in two consecutive years<sup>1,2</sup> and very positive feedback received from its members, the SCS Photochemistry Section is committed to continue their efforts in providing a platform for dissemination of latest findings and increasing the visibility of Swiss photochemical research abroad. Next activities are already being planned for 2021 and will be communicated in due course.

#### References.

- 1. https://scg.ch/pcs/2020
- 2. Kumpulainen, T.; Fürstenberg, A. Chimia 73, 840 (2019).

#### CONFERENCE ANNOUNCEMENTS

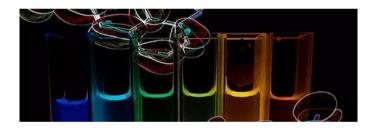


#### EPA IS ON FACEBOOK AND TWITTER





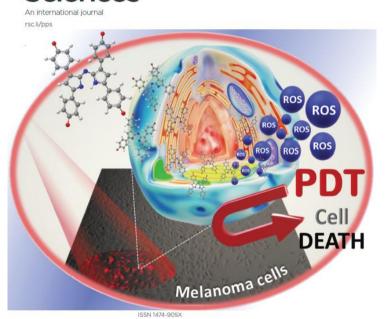
## **European Photochemistry Association**



## PHOTOCHEMICAL AND PHOTOBIOLOGICAL SCIENCES

# Photochemical & Photobiological Sciences









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