

Summary of Events: October 2010 – March 2012

Susanne Kümmel

After one and a half years since the last newsletter a lot of events have happened.

It started with the 3rd Seminar Day in Regensburg in November 2010 with interesting lectures about organocatalysis, microreactors, molecular cavities from calixarenes, photoinduced electron transfer in DNA and scientific misconduct as well as "Metallo-Supramolecular Strategies for Assembling both Discrete and Framework Molecular Structures" - a lecture from Prof. Leonard F. Lindoy from the University of Sydney.

The next event was a very interesting and interactive presentation training for the graduates held by Christine Hübner (Sprachraum, LMU Munich). The graduates practiced proper speaking and had the opportunity to present some short talk to get useful feedback from the trainer and the group.

The year 2010 closed for the GRK with a lecture of Prof. Licheng Sun from the Royal Institute of Technology in Stockholm about "Bio-inspired molecular catalysts for solar energy conversion into fuel".

In 2011 the graduate school started with two seminar days in Munich, one at the TUM with Prof. Albini, Pavia University, as a guest speaker and one organized from the LMU including the first "Graduate Intern Seminar Day" where the graduates had time to discuss their research without the supervisors in a kind of workshop. A lot of new cooperations were set up there. The seminar day continued with lectures about transient absorption spectroscopy and theoretical chemistry (Dr. Igor Pugliesi as guest speaker).

In April 2011 the graduates reported about their progress at the 6th seminar day in the "DB Trainingscenter" in Regensburg.



The next training event came up in May 2011 with the „training on scientific writing“ by Andrea Karsten (Sprachraum, LMU Munich) where the



graduates had the opportunity to learn a lot about writing styles, correct citations and also about themselves and their colleagues.

At the 7th seminar day in July 2011 Dr. Haymo Ross (Editor of the *European Journal of Organic Chemistry*) talked about scientific misconduct from the editor's point of view and Prof. David MacMillan, Princeton University, held interesting lectures about photo-organo-catalytic reactions. During the summer Taisuke Matsuno was in Regensburg as a guest researcher in the group of Prof. Reiser, the report was published in the *EuCheMS Newsletter* November 2011, page 2.

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The 8th seminar day in November 2011 started again with a graduates-only work shop in the abbey of Frauenchiemsee. Afterwards a nice workshop with Prof. Dr. Hendrik Zipse (LMU Munich) about "Radicals in Chemistry and Biology" and closed with a tutorial about "Estimation of Nucleophilicity and Electrophilicity" by Prof. Dr. Herbert Mayr (LMU Munich).



The year 2011 closed for the graduate school with a talk of Prof. Gianluca Farinola (Università degli Studi di Bari Italy) in Regensburg: with the topic "Multifunctional Organic Semiconductors".

The 9th Seminar Day was held in Regensburg in the DB-Trainingszentrum again with lectures about theoretical descriptions of photoinduced

states (Guest-Speaker: Prof. R. de Vivie-Riedle, LMU) and about intermolecular interactions including titration techniques (Dr. A. Bauer, TUM, and Prof. B. König, UR) and aggregation studies by DOSY-NMR-spectroscopy (Prof. R. Gschwind, UR). Finally a new cooperation partner of the GRK, Prof. R. Wolf, Regensburg University, introduced his research in an evening lecture.

Stay Abroad Reports

Canada, Burnaby

Michael Weinberger

The world is getting closer – so let's go there. During my Ph.D. I stayed for about three months at the Simon Fraser University in Burnaby, BC, Canada. In the group of Prof. Dr. D. Sen I wanted to use SELEX to generate a substrate binding site in my DNA based catalyst, as it is one of the major goals of the graduate college. When I arrived there, Vancouver was the most livable city in the world (now place 3 – don't blame it on me) and I definitely can say I now know why. The 2.2 million people city is at the very south west of the country, surrounded by mountains and the seaside, which offers a lot of different things to do in spare time.



Of course I needed some days to set myself up in a foreign country, but then I enjoyed the living there.

In the evenings I made a lot of inner-city trips to see a little bit of everything of the different areas in such a big metro. There is great Asian influence noticeable all over the city. This refers not only to about 30 % Chinese population. Also Indian and Japanese areas are present. Overall it must be pointed out, that the living quality can be sensed on different places. There are the sandy beaches, the quiet parks, the chilling seaside walk, the fresh aired mountains or even the beautiful downtown area with modern buildings and green areas in between. My weekend trips, sometimes inspired by or together with my lab mates, showed me the completely different area around the lively Vancouver. There I saw Canada like you imagine: beautiful autumn landscape with snow covered mountains, color changing leaves and many lakes where you hardly meet any human being, but all the more wild life.

The university in Burnaby is situated on a hill. On sunny days the look to downtown is breathtaking, but on rainy days you are right in the middle of the clouds. When you reach the top of the hill, the first impression is an American football field – I guess it has to be like that at a North American university; the buildings are also just made out of concrete. The lab itself was well equipped and the colleagues taught me how to use the different techniques in a molecular biology related research. The members of the lab were all kind and helpful at any time - not only with scientific questions, but also to make my whole stay really comfortable. To be – for a certain amount of time – a part of a foreign group gave me the opportunity to see how they run the daily lab, how they interact with their professors (and the other way round), how they handle problems. I'd like to thank my supervisor and the GRK 1626, who afforded this chance to me.

Where Do You Want Your Electrons to Go Today?

My Research Stay in the Group of Professor Wasielewski at Northwestern University

Matthias Wenninger

Only some weeks after I mentioned in a conversation with my supervisor Prof. Riedle that I am generally interested in a stay abroad within my PhD-thesis, he came back from a conference and asked me, if I am still interested I should contact Prof. Wasielewski from Northwestern University. Since the spectroscopic investigation of ultrafast inter- and intramolecular electron transfer processes was already part of my diploma thesis the research interests of the Wasielewski Group perfectly match with my own scientific interests. So I came in contact with Prof. Wasielewski and his assistant professor Dick Co. On my way home from a conference in California, where I already met PhD-students from his group in January 2011 I made a stopover in Chicago to visit the Wasielewski Group for the first time. Dick Co gave me a detailed introduction to the labs and the scientific work of the group and we made plans for my research stay in summer. So I spent the time from end of July until end of October at the Northwestern University in Illinois. The Wasielewski Group, which due to the unpronounceable name is also known as the "Waz Group", at the moment consists of two assistant professors, nine post-docs, and 15 graduate students.

The Wasielewski Group, Northwestern University, and Evanston

The Northwestern University (NU) is a private university with departments in Evanston at the beautiful lakefront of Lake Michigan and in Chicago downtown. Evanston is a relatively large suburb of Chicago with a population of roughly 74,000. The district where the university campus is located is one of the nicest districts of Evanston and is clearly dominated by students, the buildings and the life of the university.

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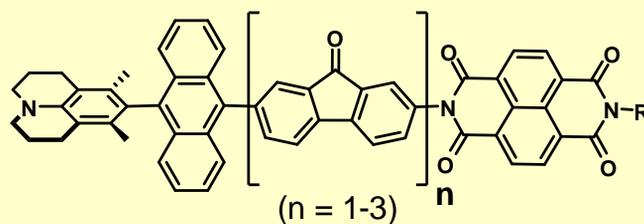
In comparison to the Ludwig Maximilian University, the NU, which was founded in 1851, is a very young university. But nevertheless the NU provides an excellent environment for students and scientists. Especially in the field of chemistry the Northwestern University, which is currently ranked 9th worldwide in chemistry (ARWU Academic Ranking of World Universities, also known as Shanghai Ranking, in Chemistry - 2011), belongs to the leading universities of the world.

My Scientific Work

Light induced charge separation is one of the most important processes when light serves as driving force for catalytic processes. However, fast recombination of the photo-induced charge separated state often inhibits photocatalysis with a high quantum yield. Especially when the catalytic reaction is limited by diffusion, the life time of the catalytically active charge separated state is often too short for efficient electron transfer reactions between photocatalyst and substrate. Hence it is essential to establish strategies to achieve long-lived light-induced charge separated states. One approach is to generate a charge separated triplet state which is long-lived due to the spin-forbidden charge recombination. The well-investigated flavin sensitized photo-oxidation of benzyl alcohol, where the intermolecular charge separated triplet state serves as the key state for the catalytic reaction, is an illustrative example for the application of this strategy. Another approach is the photo-induced transfer of an electron from the electron donating chromophore to the catalytically active centre of the molecule, which is some distance away. This charge separated state is long-lived due to the slow charge recombination of electron and hole over a large distance. To control and optimize the photo-induced charge separation, the consolidated knowledge of the physics of the molecular charge transfer process is indispensable. To understand

the photo-induced electron transfer processes in molecules is one of the core objectives of the group of Prof. Wasielewski. The group combines methods of synthesis, time resolved spectroscopy and electron parametric resonance, spectroelectrochemistry, and theoretical chemistry together under one roof.

My scientific work during my stay was focused on the spectroscopic investigation of the photo-induced electron transfer in a donor-bridge-acceptor system (DBA), where a 3,5-dimethyl-4-(9-anthracenyl)-julolidine chromophore and a naphthalene-1,8:4,5-bis(dicarboximide) (NI) acceptor are linked by oligomeric 2,7-fluorenone (FN)_n bridges (see figure). We were using time resolved spectroscopy in the visible and infrared spectral range and femtosecond stimulated Raman spectroscopy to investigate the electron transfer over the fluorenone bridge molecules.



As expected for different bridge lengths (n=1-3) the rate of the electron transfer decreases with increasing distance between donor and acceptor. Marcus theory predicts an exponential dependence on the distance which can be described with an attenuation factor b . In the literature, a high beta value is assigned to a coherent tunneling mechanism through the nearly insulating bridge (superexchange), whereas a low beta value is assigned to an incoherent hopping electron transfer mechanism through the well conducting bridge. Although we observed a relatively high beta value of $b = 0.34 \text{ \AA}^{-1}$ in the present DBA-system, we were able to observe incoherent hopping of the electron through the bridge.

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Usually for a beta-value of $b = 0.34 \text{ \AA}^{-1}$ one would expect a coherent superexchange mechanism of the electron through the bridge molecules. Especially the comparison of the species associated spectra (SAS), which we obtained from the measured transient absorption data with the spectra of the reduced fluorenone which were determined with the help of spectroelectrochemistry was a big step towards a full understanding of the transient kinetics. The results of the study were submitted to the Journal of the American Chemical Society and were accepted for publication on February 15th:

Annie Butler Ricks, Dick T Co, Kristen E Brown, Matthias K Wenninger, Steven D Karlen, Yuri A Berlin, and Michael R Wasielewski, "Exponential Distance Dependence of Photoinitiated Stepwise Electron Transfer in Donor-Bridge-Acceptor Molecules: Implications for Wire-like Behavior" (<http://pubs.acs.org/doi/abs/10.1021/ja205913q>)

Recent Publications

- Uwe Megerle, Robert Lechner, Burkhard König and Eberhard Riedle; *Photochem. Photobiol. Sci.* **2010**, 9 (10), 1400-1406.
- Emanuel Peter, Bernhard Dick and Stephan A. Baeurle; *Nature Communications* **2010**, 1 (8), 122.
- Robert Lechner, Susanne Kümmel, Burkhard König; *Photochem. Photobiol. Sci.* **2010**, 9, 1367-1377.
- M. Neumann, S. Földner, B. König, K. Zeitler*; *Angew. Chem. Int. Ed.* **2011**, 50, 951-954.
- Tapan Maji, Ananta Karmakar, Oliver Reiser*; *J. Org. Chem.* **2011**, 76, 736-739.
- Stefan Földner, Patrick Pohla, Hanna Bartling, Stephan Dankesreiter, Roland Stadler, Michael Gruber, Arno Pfitzner, Burkhard König; *Green Chem.* **2011**, 13, 640-643.
- Stefan Földner, Tatiana Mitkina, Tobias Trottmann, Alexandra Frimberger, Michael Gruber, Burkhard König*; *Photochem. Photobiol. Sci.* **2011**, 10, 623-625.

- Uwe Megerle, Matthias Wenninger, Roger-Jan Kutta, Robert Lechner, Burkhard König, Bernhard Dick, Eberhard Riedle; *Physical Chemistry Chemical Physics* **2011**, 13, 8869-8880.
- Matthias Wenninger, Danila Fazio, Uwe Megerle, Christian Trindler, Stefan Schiesser, Eberhard Riedle, Thomas Carell; *ChemBioChem* **2011**, 12, 703-706.
- E. Peter, Bernhard Dick, Stephan A. Baeurle; *J. Chem. Biol.* **2011**, 4 (4), 167-184.
- Durga Prasad Hari and Burkhard König*; *Org. Lett.* **2011**, 13 (15), 3852-3855.
- Thomas Merz, Keyarash Sadeghian and Martin Schütz; *Phys. Chem. Chem. Phys.* **2011**, 13, 14775-14783.
- E. Peter, B. Dick, S. A. Baeurle; *J. Mol. Mod.* **2011**, in press.
DOI: 10.1007/s00894-011-1165-6
- Günther Knör and Uwe Monkowius in Rudi van Eldik and Grazyna Stochel, editors: *Advances in Inorganic Chemistry*, Vol. 63, Burlington: Academic Press, 2011, pp. 235-289.
- Emanuel Peter, Bernhard Dick, Stephan A. Baeurle; *Proteins* **2012**, 80 (2), 471-481.
- C. Müller, A. Bauer, M. M. Maturi, M. C. Cuquerella, M. A. Miranda, T. Bach; *J. Am. Chem. Soc.* **2011**, 133, 16689-16697.
- Emanuel Peter, Bernhard Dick, Stephan A. Baeurle; *Proteins* **2012**, in press.
DOI: 10.1002/prot.24031
- Paul Kohls, Deepak Jadhav, Ganesh Pandey, Oliver Reiser; *Org. Lett.* **2012**, 14 (3), pp 672-675.

Upcoming events

- 21.03.2012** – Talk: Prof. Petr Klán
25.-27.04.2012 – 10th Seminar Day in Munich
04.06.2012 – Lecture: Prof. Sascha Ott
13.06.2012 – Talk: Prof. Pablo Wessig
19.-20.6.2012 – 11th Seminar Day in Blaubeuren

Further information will be published timely on our web-page.