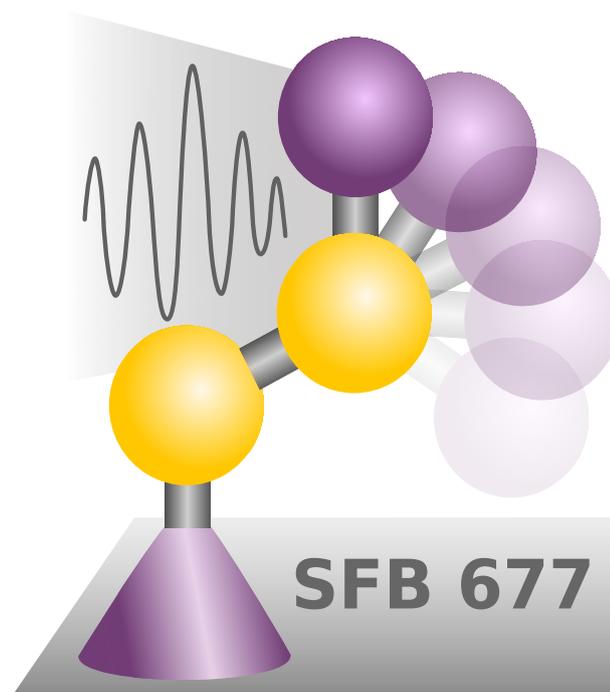


Fourth SFB Conference

Molecular Switches: Elementary Processes and Applications

August 25 - 28, 2019

Fielmann Akademie, Schloss Plön



CONFERENCE INFORMATION

BOOK OF ABSTRACTS

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GENERAL INFORMATION

Conference Secretary Phone No.

+49 1520 3181298

Venue Contact Information

Fielmann Akademie Schloss Plön

Hotel- und Catering GmbH

24306 Plön

phone: +49 4522 8010

fax: +49 4522 801111

e-mail: info@fielmann-akademie.com

Notice

The editorial deadline for this book of abstracts was on August 21. For more recent information and schedule updates please see our conference website at:

www.sfb677.uni-kiel.de

→ [Events] → [Plön 2019]

VENUE

The fourth SFB conference "Molecular Switches: Elementary Processes and Applications" will be held at Plön Castle, which is located in the heart of the Holstein lake district.

- built 1633-1636 by Duke Joachim Ernst of Sonderburg-Plön
- Ducal residence since 1636
- Royal Danish summer residence since 1761
- Royal Prussian cadet academy since 1868
- Academy for the sons of Emperor Wilhelm II since 1896



Plön Castle



2nd SFB Conference 2012

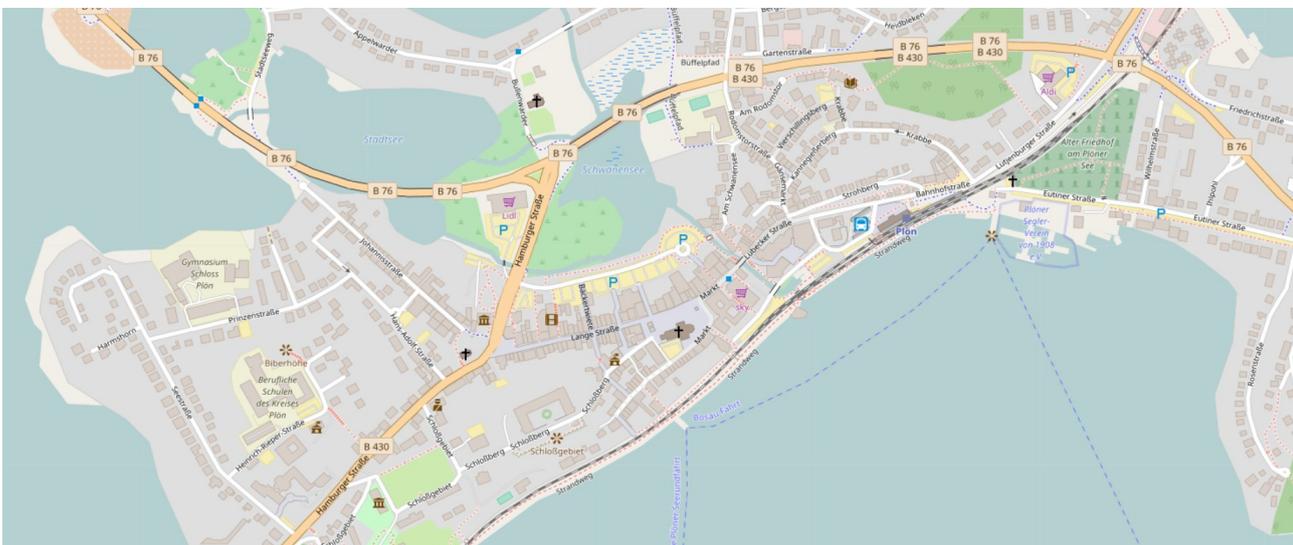
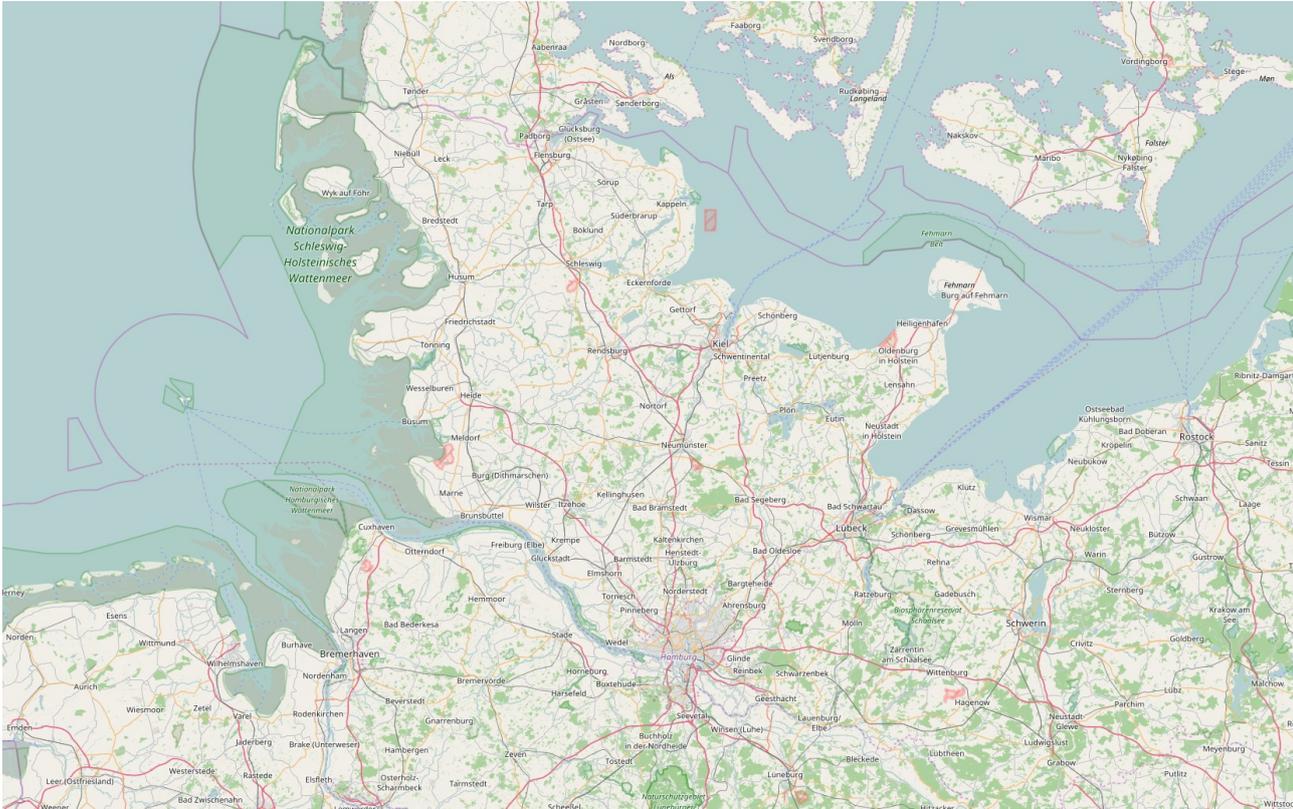


lecture hall



boat excursion

LOCATION



SHORT SCHEDULE

Sunday, 25. Aug. 2019		Monday, 26. Aug. 2019			Tuesday, 27. Aug. 2019			Wednesday, 28. Aug. 2019						
	07:00	breakfast		07:00	breakfast		07:00	breakfast						
	09:00	Wöll	Karlsruhe	chair: Herges	09:00	Rück-Braun	Berlin	chair: Magnussen	09:00	Kaleta	Prag	chair: Berndt		
	09:30	A03	Kiel		09:30	Jacquemin	Nantes		09:30	B12	Kiel			
	09:50	B09	Kiel		10:00	C12	Kiel		09:50	B07	Kiel			
	10:10	Planowski	Karlsruhe		10:20	A01	Kiel		10:10	C13	Kiel			
	10:40	coffee break 11:00 – 11:30		10:40	coffee break 11:00 – 11:30		10:30	coffee break 10:30 – 11:00						
	11:30	A07	Kiel	chair: Herges	11:30	Meerholz	Köln	chair: Faupel	11:00	B06	Kiel	chair: Herges		
	11:50	B11	Kiel		12:00	Ihmels	Siegen		11:20	A06	Kiel			
	12:10	König	Regensb.		12:30	A08	Kiel		11:40	B10	Kiel			
	12:50	lunch 13:00 - 14:00		12:50	lunch 13:00 - 14:00		12:50	lunch 13:00 - 14:00		12:00	Dommaschk	Manchester		
	14:00 – 16:00	poster session		14:00	Bäuerle	Ulm	chair: Berndt	12:30	closing remarks		Herges			
	16:00	Wulfkekel	Karlsruhe	chair: Magnussen	14:30	C14	Kiel	12:45	lunch departure					
	16:30	B13	Kiel		14:50	Dube	München	14:00						
	16:50	C01	Kiel		15:30 departure 16:00 – 18:00 boat excursion									
	17:10	Schull	Strasbourg		conference dinner									
	17:40	Krüger	Würzburg											
	19:30	dinner		19:30										
13:00	arrival													
16:00	registration													
18:00	welcome party													
19:30	dinner													

DETAILED SCHEDULE**Sunday, 25.08.2019**

- 13:00 *arrival*
16:00 *registration*
18:00 *welcome reception*
19:30 *dinner*

Monday, 26.08.2019

- 07:00 *breakfast*
09:00 ***Christof Wöll, Karlsruhe, Germany***
Implementing, Characterizing, and Utilizing Molecular Switches: The SURMOF Approach
09:30 ***SFB 677 project A3, Leonie Fitschen, Tammy Jacobsen-Bialas, Kiel***
New spin crossover complexes for spin switching in solution and on surfaces
09:50 ***SFB 677 project B9, Rainer Herges, Kiel***
Switching Adsorbate Layers Based on the Platform Concept
10:10 ***Zbigniew Lech Pianowski, Karlsruhe, Germany***
Photochromic peptides for visible-light-triggered hydrogels and beyond
10:40 *coffee break*
11:30 ***SFB 677 project A7, Bernd Hartke, Kiel***
Dynamics of Intramolecular H-Transfer Photoswitches
11:50 ***SFB 677 project B11, Thisbe K. Lindhorst, Kiel***
Sweet Switches
12:10 ***Burkhard König, Regensburg, Germany***
Photoswitches in Photopharmacology: The good, the bad and the ugly
12:40 *lunch*
14:00 *poster session*
16:00 ***Wulf Wulfhekel, Karlsruhe, Germany***
Making the Tiniest Machines
16:30 ***SFB 677 project B13, Kai Rossnagel, Felix Tuczek, Kiel***
Photoswitchable spin-crossover films on ferromagnetic substrates

- 16:50 **SFB 677 project C1, Franz Faupel, Kiel**
Photoswitchable Metal-Polymer Nanocomposites
- 17:10 **Guillaume Schull, Strasbourg, France**
Fluorescence microscopy with sub-molecular resolution with STM
- 17:40 **Anke Krueger, Würzburg, Germany**
Functionalization of nanodiamond for the control of electronic surface properties
- 19:30 **dinner**

Tuesday, 27.08.2019

- 07:00 **breakfast**
- 09:00 **Karola Rück-Braun, Berlin, Germany**
Light-controlled interactions of fluorophore-DAE conjugates linked to titanium dioxide surfaces
- 09:30 **Dennis Jacquemin, Nantes, France**
Understanding multi-photochromes with theory
- 10:00 **SFB 677 project C12, Dorian Schmidt, Kiel**
Photoswitchable Protein Kinase Inhibitors for Novel Anti-Cancer Applications
- 10:20 **SFB 677 project A1, Falk Renth, Kiel**
Ultrafast Dynamics of Photo-induced Switching Processes
- 10:40 **coffee break**
- 11:30 **Klaus Meerholz, Köln, Germany**
Solution-Processed Organic Semiconductors and their Applications
- 12:00 **Heiko Ihmels, Siegen, Germany**
Controlling ligand-DNA interactions with light: The search for photoswitchable DNA intercalators
- 12:30 **SFB 677 project A8, Daniel Hugenbusch, Fabian Kruse, Kiel**
Molecular Assemblers: Light Driven Molecular Machines for Synthesis
- 12:50 **lunch**
- 14:00 **Peter Bäuerle, Ulm, Germany**
Synthetic approaches towards 2D- and 3D-thiophene-based nanomaterials

- 14:30 **SFB 677 project C14, Rainer Adelung, Kiel**
Mechanophoric Composites
- 14:50 **Henry Dube, München, Germany**
Indigoid Photoswitches - Visible Light Responsive Molecular Tools
- 15:30 **departure for excursion**
- 16:00 **boat excursion**
- 19:30 **conference dinner**

Wednesday, 28.08.2019

- 07:00 **breakfast**
- 09:00 **Jiří Kaleta, Prague, Czech Republic**
Reversible photochromism in the cavities of flexible coordination cages
- 09:30 **SFB 677 project B12, Michael Bauer, Kiel**
Control of Surface Plasmon Polariton Propagation by Molecular Switches
- 09:50 **SFB 677 project B7, Manuel Gruber, Kiel**
Switching the spin of single molecules on surfaces
- 10:10 **SFB 677 project C13, Jonas Warias, Kiel**
X-Ray Reflectivity Investigation of Structure and Kinetics of Photoswitchable Lipid Monolayers
- 10:30 **coffee break**
- 11:00 **SFB 677 projects B6, Richard Berndt, Kiel**
STM/STS of bistable molecules
- 11:20 **SFB 677 project A6, Vanessa Wellm, Jens Gröbner, Kiel**
Switchable Contrast Agents for Magnetic Resonance Imaging
- 11:40 **SFB 677 project B10, Stefan Heinze, Kiel**
First-principles study of tip-adsorbate interactions in scanning probe experiments
- 12:00 **Marcel Dommaschk, Manchester, UK**
Dynamic Control of Chiral Space in a Rotaxane Organocatalyst
- 12:30 **closing remarks**
- 12:45 **lunch**
- 14:00 **departure**

LIST OF PARTICIPANTS

Prof. Dr. Rainer Adelung, Kiel, Germany
Prof. Dr. Michael Bauer, Kiel, Germany
Prof. Dr. Peter Bäuerle, Ulm, Germany
Birthe Behr, Kiel, Germany
Prof. Dr. Richard Berndt, Kiel, Germany
Dr. Claus Bier, Kiel, Germany
Christoph Bohl, Kiel, Germany
Maximilian Heiko Burk, Kiel, Germany
Dr. Marcel Dommaschk, Manchester, United Kingdom
Dr. Henry Dube, München, Germany
Prof. Dr. Mady Elbahri, Aalto, Finland
Julia Ewert, Kiel, Germany
Ellen Fast, Kiel, Germany
Prof. Dr. Franz Faupel, Kiel, Germany
Kim Fischer, Kiel, Germany
Leonie Fitschen, Kiel, Germany
Benedikt Flöser, Kiel, Germany
Dr. Ling Fu, Kiel, Germany
Prof. Dr. Jens Gröbner, Lüdenscheid, Germany
Dr. Manuel Gruber, Kiel, Germany
Jan Grunwald, Kiel, Germany
Sebastian Hamer, Kiel, Germany
Prof. Dr. Bernd Hartke, Kiel, Germany
Svenja Hövelmann, Kiel, Germany
Prof. Dr. Stefan Heinze, Kiel, Germany
Prof. Dr. Rainer Herges, Kiel, Germany
Rebecca Holtmann, Kiel, Germany
Daniel Hugenbusch, Kiel, Germany
Prof. Dr. Heiko Ihmels, Siegen, Germany
Tammy Jacobsen-Bialas, Kiel, Germany
Prof. Dr. Denis Jacquemin, Nantes, France
Torben Jäkel, Kiel, Germany
Sven Johannsen, Kiel, Germany
Nafise Kalantari, Kiel, Germany
Dr. Jiří Kaleta, Prague 6, Czech Republic
Dr. Matthias Kalläne, Kiel, Germany
Prof. Dr. Burkhard Koenig, Regensburg, Germany
Dr. Oliver Koepler, Hannover, Germany
Nicolai Krekieh, Kiel Deutschland
Prof. Dr. Anke Krueger, Würzburg, Germany
Fabian Kruse, Kiel, Germany
Prof. Dr. Ulrich Lüning, Kiel, Germany
Clemens Lütjohann, Kiel, Germany
Marc Lehr, Kiel, Germany
Pascal Lentès, Kiel, Germany
Shuo Li, Kiel, Germany
Prof. Dr. Thisbe Lindhorst, Kiel, Germany
Jannis Ludwig, Kiel, Germany
Prof. Dr. Olaf Magnussen, Kiel, Germany
Prof. Dr. Anna McConnell, Kiel, Germany
Prof. Dr. Klaus Meerholz, Cologne, Germany
Sebastian Megow, Kiel, Germany
Dr. Elena Mena-Osteritz, Ulm, Germany
Tobias Moje, Kiel, Germany
Dr. Bridget Murphy, Kiel, Germany
Sascha Ossinger, Kiel, Germany
Tobias Paschelke, Kiel, Germany
Pascal Pessier, Kiel, Germany
Dr. Zbigniew Pianowski, Karlsruhe, Germany
Dr. Tim Raeker, Kiel, Germany

Dr. Falk Renth, Kiel, Germany

Sebastian Rohlf, Kiel, Germany

Prof. Dr. Kai Rossnagel, Kiel, Germany

Prof. Dr. Karola Rueck-Braun, Berlin, Germany

Alexander Schlimm, Kiel, Germany

Dorian Schmidt, Kiel, Germany

Dr. Guillaume Schull, Strasbourg, France

Mathias Schulz, Kiel, Germany

Bill Brook Shurtleff, Kiel, Germany

Insa Stamer, Kiel, Germany

Dr. Thomas Strunskus, Kiel, Germany

Prof. Dr. Felix Tuczek, Kiel, Germany

Jan-Robert Vogt, Kiel, Germany

Jan-Simon von Glasenapp, Kiel, Germany

Wiebke Wagner, Kiel, Germany

Jonas Warias, Kiel, Germany

Prof. Dr. Christof Wöll, Karlsruhe, Germany

Vanessa Wellm, Kiel, Germany

Dr. Torsten Winkler, Kiel, Germany

Prof. Dr. Wulf Wulfhekel, Karlsruhe, Germany

ABSTRACTS FOR INVITED LECTURES

in alphabetical order of presenters

Synthetic approaches towards 2D- and 3D-thiophene-based nanomaterials

T. Leitner, Y. Gmeinder, E. Mena-Osteritz, P. Bäuerle

Institute of Organic Chemistry II and Advanced Materials/University of Ulm, Albert-Einstein-Allee 11, 89081 Ulm, Germany, peter.baeuerle@uni-ulm.de

Oligothiophenes represent an important class of compounds in the field of organic semiconductors and organic electronics. On the basis of thiophenes, we are currently synthesizing and investigating novel conjugated architectures and shapes, such as linear, macrocyclic, dendritic, or fused.

In particular, we have recently developed series of novel S,N-heteroacenes up to a 13-mer which combine the stability of oligothiophenes and the planar extended π -system of (phen)acenes.¹ Conjugated materials with highly interesting optoelectronic properties,² small bond length alternation, planarity, and good charge transport properties qualify them for application in highly efficient organic³ and perovskite solar cells.⁴ This class of compounds has now been extended to corresponding selenophene and silole-containing heteroacenes.

Opposite to the flat heteroacenic structures, we started to develop and synthesize three-dimensional and sterically crowded thienylene-phenylene structures.

1. C. Wetzel, E. Brier, A. Vogt, A. Mishra, E. Mena-Osteritz, P. Bäuerle, *Angew. Chem. Int. Ed.* **2015**, *54*, 12334;
2. C. Wetzel, A. Vogt, A. Rudnick, E. Mena-Osteritz, A. Köhler, P. Bäuerle, *Org. Chem. Front.* **2017**, *4*, 1629-1635;
3. T. Leitner, A. Vogt, D. Popović, E. Mena-Osteritz, K. Walzer, M. Pfeiffer, P. Bäuerle, *Mater. Chem. Front.*, **2018**, *2*, 959-968;
4. D. Bi, A. Mishra, P. Gao, M. Franckevicius, C. Steck, S. M. Zakeeruddin, M. K. Nazeeruddin, P. Bäuerle, M. Grätzel, A. Hagfeldt, *ChemSusChem*, **2016**, *9*, 433-438.

Dynamic Control of Chiral Space in a Rotaxane Organocatalyst

Marcel Dommaschk

Whether or not an object has a superimposable mirror image is formally a binary issue. However, it is the extent to which chirality is expressed on the space surrounding a molecular structure that is generally important for the effective transmission of asymmetry. This work reports rotaxane organocatalysts whose chiral expression is controlled by shuttling of the macrocycle. The process can be exploited to enhance the effective asymmetry and to change the apparent handedness of the environment around a catalytic site. It is the first example for the dynamic control of the facial bias in organocatalysis using a rotaxane.

Indigoid Photoswitches - Visible Light Responsive Molecular Tools

Henry Dube

LMU München, Butenandtstr. 5-13, 81377 München

Indigoid chromophores are a class of emerging photoswitches with many advantages for applications. However, despite their high potential as versatile and efficient molecular triggering unit, they have been largely overlooked by material sciences as well as supramolecular and biological chemistry. In the recent years, we have explored the interesting photophysical properties of indigoid photoswitches in depth and developed a thorough mechanistic understanding of their light induced motions and behavior in the excited state. We use this fundamental knowledge to build next generation molecular machines and responsive supramolecular systems with unprecedented properties. Our main goal is to develop smart molecular entities, which can conveniently be implemented into more complex architectures to manipulate matter at the molecular scale with the highest possible precision.

Controlling ligand-DNA interactions with light: The search for photoswitchable DNA intercalators

Heiko Ihmels

Department of Chemistry-Biology, University of Siegen, Germany

E-Mail: ihmels@chemie.uni-siegen.de

The association of ligands with nucleic acids is an important process in biology and in medicine, because it usually induces a significant change of the DNA structure. As a result, the formation of ligand-DNA complexes may have a fundamental influence on the physiological function of the nucleic acid, so that DNA binders are traditionally considered as potential lead structures in anti-cancer approaches.¹ In this context, it is desirable to accomplish spatial and temporal control of the ligand-DNA interaction in order to increase the selectivity and efficiency. For that purpose, the application of light to trigger the DNA-binding event offers several distinct advantages, because light is non-invasive, traceless, and easy to apply. Indeed, specifically modified photochromic ligands have been reported that bind to DNA with only one of the components of the photochromic equilibrium, so that the association with DNA may be controlled by light.² In our efforts to assess the structural parameters that govern the association of cationic azoniahetarenes with nucleic acids³ we also examined concepts to accomplish a photo-induced complexation of photoactive substrates.⁴ Specifically, we applied electrocyclization reactions of spirooxazines, chromenes and styrylpyridines as well as reversible photocycloaddition reactions of styrylquinolinium and benzo[b]quinolinium derivatives to generate DNA ligands upon irradiation. In this contribution, the main results of these studies will be presented and discussed with a special emphasis on the trade-off between appropriate photochromic properties and sufficient affinity of the ligand unit toward DNA.

1. S. Neidle, D. E. Thurston, *Nat. Rev. Cancer* 2005, 5, 285.

2. Representative examples. Spiropyran: a) J. Andersson, S. Li, P. Lincoln, J. Andréasson, *J. Am. Chem. Soc.* 2008, 130, 11836; b) C. Brieke, A. Heckel, *Chem. Eur. J.* 2013, 19, 15726. Stilbenes: C. G. Fortuna, U. Mazzucato, G. Musumarra, D. Pannacci, A. J. Spalletti, *Photochem. Photobiol. A* 2010, 216, 66. Azobenzenes: a) C. Dohno, S.-N. Uno, K. Nakatani, *J. Am. Chem. Soc.* 2007, 129, 11898. b.) A. Basak, D. Mitra, M. Kar, K. Biradha, *Chem. Commun.* 2008, 3067. c) X. Wang, J. Huang, Y. Zhou, S. Yan, X. Weng, X. Wu, M. Deng, X. Zhou, *Angew. Chem.* 2010, 122, 5433. Dithienylethenes: A. Mamma, G. T. Carroll, J. Areephong, B. L. Feringa, *J. Phys. Chem. B* 2011, 115, 11581.

3. A. Granzhan, H. Ihmels, *Synlett* 2016, 27, 1775.

4. a) S. V. Paramonov, V. Lokshin, H. Ihmels, O. A. Fedorova, *Photochem. Photobiol. Sci.* 2011, 10, 1279. b) H. Ihmels, J. Mattay, F. May, L. Thomas, *Org. Biomol. Chem.* 2013, 11, 5184. c) D. V. Berdnikova, T. M. Aliyev, T. Paululat, Y. V. Fedorov, O. A. Fedorova, H. Ihmels, *Chem. Commun.* 2015, 51, 4906. d) A. Bergen, S. Rudiuk, M. Morel, T. Le Saux, H. Ihmels, D. Baigl, *ACS Nanolett.* 2016, 16, 773

Understanding multi-photochromes with theory

Denis Jacquemin

Laboratoire CEISAM -UMR CNR 6230, Université de Nantes, 2 Rue de la Houssinière, BP 92208, Nantes 44322, France, Tel: +33-2-51125564; E-mail: Denis.Jacquemin@univ-nantes.fr

To go beyond the binary operations offered by photochromic compounds, building multiphotochromes, that is molecules encompassing several photochromic units, is an appealing strategy. Though numerous multiphotochromes have been synthesized during the last decade, most are subject to drastic limitations [1]. For instance, in multi-diarylethenes, it is a common outcome that only one of the photochromes is experimentally active [1,2]. As a consequence, conceiving efficient and useful multiphotochromes remains an important challenge, and theoretical tools might be useful to tackle this challenge. In this talk, I will show why multiphotochromes tend to be less reactive than their constitutive parts using a curve-crossing model that is displayed in Figure 1. Indeed, extra crossing points, not present in isolated photochromes, appear in multiphotochromes, hampering the reactivity [3]. I will discuss strategies that can be used to circumvent this limitation [3,4]. Next, using selected examples, I will show that several criteria (structures, energies, topologies of the orbitals and crossing points, etc.) may play a role in the reactivity of multidarylethenes. Finally, I will show that surface can be used to break the symmetry of the systems and improve or not performances [5-7].

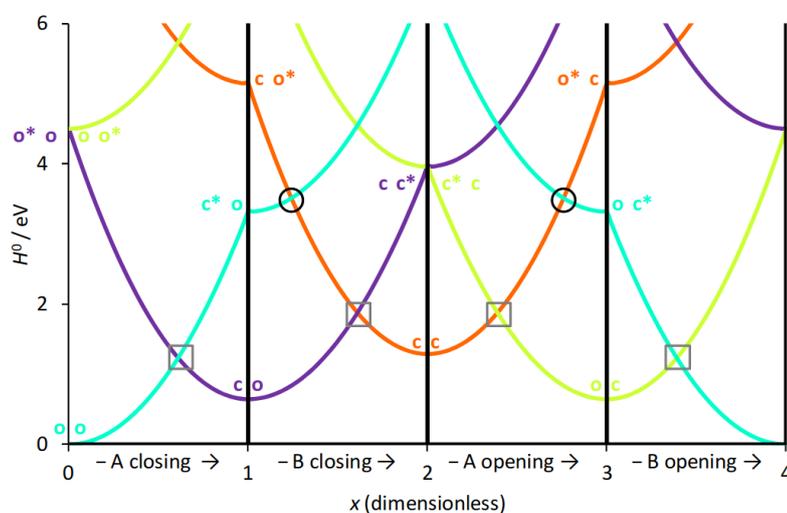


Figure1. Curvecrossing model for a diarylethene dimer.

Reference

1. Fihey, A.; Perrier, A.; Browne, W.R.; Jacquemin, D. *Chem. Soc. Rev.* 2015, 44, 3719.
2. Perrier, A.; Maurel, F.; Jacquemin, D. *Acc. Chem. Res.* 2012, 45, 1173.
3. Lasorne, F.; Fihey, A.; Mendive-Tapida, D.; Jacquemin, D. *Chem. Sci.* 2015, 6, 5695.
4. Fihey, A.; Jacquemin, D. *Chem. Sci.* 2015, 6, 3495.
5. Chen, K.J.; Boucher, F.; Jacquemin, D. *J. Phys. Chem. C* 2015, 119, 16860.
6. Belhboub, A.; Boucher, F.; Jacquemin, D. *J. Phys. Chem. C* 2016, 120, 18281.
7. Belhboub, A.; Boucher, F.; Jacquemin, D. *J. Mater. Chem. C* 2017, 5, 1624.

Regular 2-D Films Of Molecular Machines

Jiří Kaleta

Institute of Organic Chemistry and Biochemistry of the CAS, Flemingovo nám. 2, 166 10 Prague 6, Czech Republic, kaleta@uochb.cas.cz

Controlled attachment of various molecular machines (motors, rotors, and switches) to flat surfaces is an attractive and promising route towards new generation of highly ordered 2-D materials. Organization of individual molecules into regular arrays (Figure 1) should among others amplify their function and lead to the new types of smart materials with potential application for example in nanoelectronics. Several approaches leading to such systems built on solid-gas^{1,2} and liquid-gas^{3,4} interphases will be discussed.

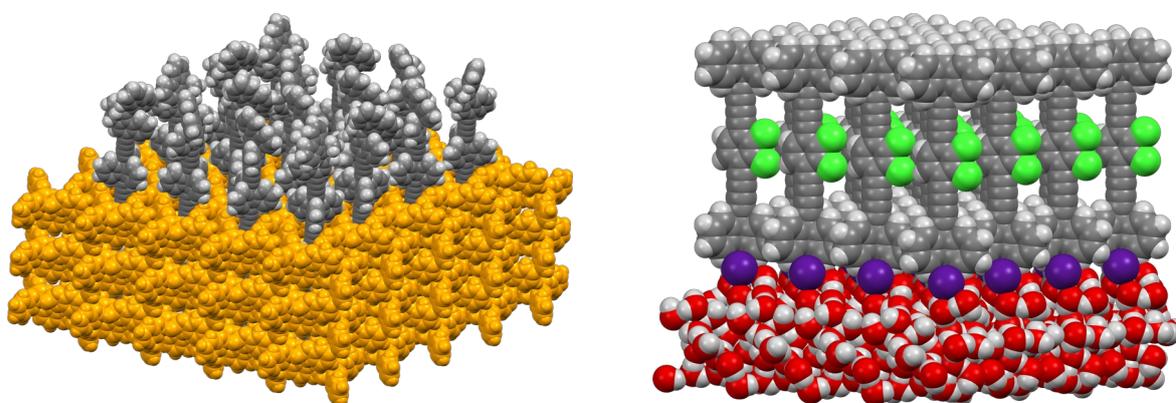


Figure 1: Regular array of molecular motors (left) and rotors (right).

[1] Kaleta, J.; Dron, P. I.; Zhao, K.; Shen, Y.; Císařová, I.; Rogers, C. T.; Michl, J. *J. Org. Chem.* **2015**, *80*, 6173-6192.

[2] Kaleta, J.; Chen, J.; Bastien, G.; Dračinský, M.; Mašát, M.; Rogers, C. T.; Feringa, B. L.; Michl, J. *J. Am. Chem. Soc.* **2017**, *139*, 10486-10498.

[3] Kaleta, J.; Kaletová, E.; Císařová, I.; Teat, S. J.; Michl, J. *J. Org. Chem.* **2015**, *80*, 10134-10150.

[4] Kaleta, J.; Wen, J.; Magnera, T. F.; Dron, P. I.; Zhu, C.; Michl, J. *PNAS* **2018**, *115*, 9373-9378.

Photoswitches in Photopharmacology: The good, the bad and the ugly

Burkhard König

Faculty of Chemistry and Pharmacy, University of Regensburg, 93040 Regensburg, Germany; email: burkhard.koenig@ur.de

Visible light is a fascinating reagent: It provides energy for chemical transformations, can be selectively delivered to a specific molecule and leaves no trace even if applied in large excess. The three typically classes of photochromic molecules in decreasing order of their use are azobenzenes,¹ dithienylethenes and fulgides. Different photoswitches have specific advantages and disadvantages for applications in photopharmacology. We discuss their properties with recent examples from our laboratory aiming at photochromic enzyme inhibitors,² ligands of G-protein coupled receptors,³ redox mediators⁴ and ion channel modulators.

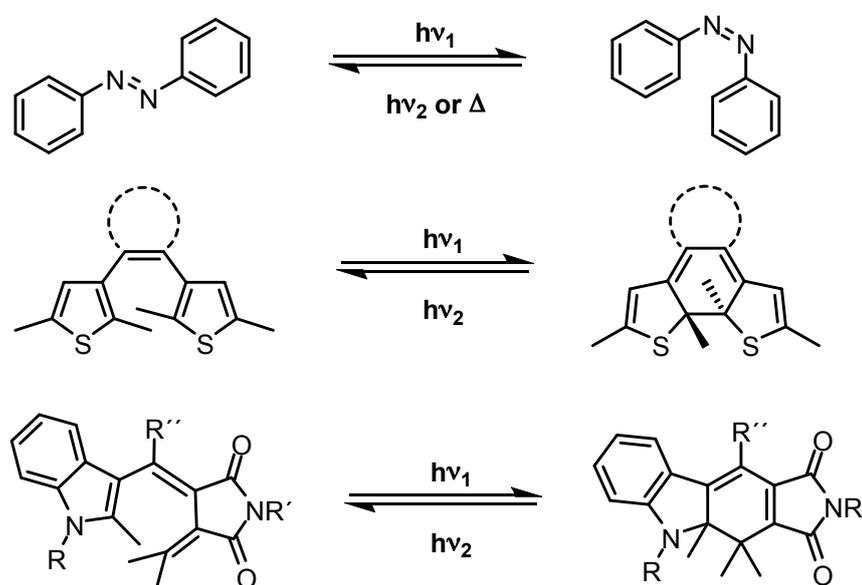


Figure 1. Typical photoswitches in photopharmacology

References

1. Simeth, N. A.; Crespi, S.; Fagnoni, M.; König, B. *J. Am. Chem. Soc.* **2018**, *140*, 2940.
2. Reisinger, B.; Kuzmanovic, N.; Löffler, P.; Merkl, R.; König, B.; Sterner, R. *Angew. Chem. Int. Ed.* **2014**, *53*, 595.
3. Lachmann, D.; Studte, C.; Männel, B.; Hübner, H.; Gmeiner, P.; König, B. *Chem. Eur. J.* **2017**, *23*, 13423.
4. Simeth, N. A.; Kneuttinger, A. C.; Sterner, R.; König, B. *Chem. Sci.* **2017**, *8*, 6474.

Acknowledgements

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Functionalization of nanodiamond for the control of electronic surface properties

Benjamin Kiendl,¹ Johannes Ackermann,¹ Michael Drisch,² Fabian Keppner,² Benedikt Knichelmann,¹ Amélie Venerosy,³ Hugues Girard,³ Jean-Charles Arnault,³ Karin Larsson,⁴ Maik Finze,² Ann-Christin Pöppler,¹ Anke Krueger¹

¹ Institut für Organische Chemie, Julius-Maximilians-Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany;

² Institut für Anorganische Chemie, Julius-Maximilians-Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany;

³ CEA, LIST, Diamond Sensors Laboratory, Bâtiment 451, PC 45, 91191 Gif sur Yvette, France;

⁴ Angström Laboratory, Uppsala University, Lägerhyddsvägen 1, Uppsala, Sweden

The surface chemistry of solid state materials plays a crucial role for their electronic properties. For carbon materials the surface chemistry is very rich and can be used to control the properties in a very broad range, i.e. the electron affinity of the surface[1] or the control of charge states of lattice defects[2].

The change from electron withdrawing to donating surface groups influences the charge state of lattice defects close to the surface. Additionally, the band structure of the material is strongly depending on the surface termination. Therefore, the homogeneous and stable surface functionalization with suitable atoms or groups is key for the fabrication of diamond based devices for e.g. photocatalytic or quantum applications.

Here we report on the efficient surface termination of diamond different surface groups. These treatments lead to highly functionalised surfaces that enable the stabilisation of negative charge states of lattice defects as well as the control of the electron affinity of the surface.

Characterisation using e.g. solid-state NMR techniques and Boehm titration have been used to analyse the functionalised materials qualitatively and quantitatively.

This research has received funding from the European Union's Horizon 2020 Programme (Grant Agreement no. 665085, DIACAT, www.diacat.eu) and Deutsche Forschungsgemeinschaft under grant KR3316/6-2.

References

[1] D. Zhu, J. A. Bandy, S. Li, R. J. Hamers, *Surf. Sci.* 650, 295 (2016)

[2] S. Cui, E. L. Hu, *Appl. Phys. Lett.* 103, 051603 (2013)

Solution-Processed Organic Semiconductors and their Applications

Klaus Meerholz

University of Cologne, Germany

Organic light emitting diodes (OLEDs) based on electroluminescent conjugated polymers are considered as a promising alternative for display and lighting applications, mainly due to their better compatibility with low-cost production techniques and large substrates. A challenge is multiple-layer deposition to improve the efficiency of the devices and, as a result, their lifetime.

This lecture introduces recent trends in the field of OLED with an emphasis on solution-processed devices. We have in the past developed photochemically crosslinkable semiconductors for fabrication of complex multilayer OLED ^[1] with a potential for eventually becoming organic lasers ^[2] and RGB-pixelation. ^[3,4] Recently, we also introduced organic memories (OMEM) with multi-bit storage capacity. ^[5,6]

[1] C.D. Müller, A. Falcou, N. Reckefuss, M. Rojahn, V. Wiederhirn, P. Rudati, H. Frohne, O. Nuyken, H. Becker, K. Meerholz, *Nature* 421, 829 (2003).

[2] B.H. Wallikewitz, M. de la Rosa, J.H.W.M. Kremer, D. Hertel, K. Meerholz, *Adv. Mat.*, 22, 531 (2010).

[3] M.C. Gather, A. Köhnen, A. Falcou, H. Becker, Klaus Meerholz, *Adv. Funct. Mat.* 17, 191 (2007).

[4] F. Ventsch, M.C. Gather, K. Meerholz, *Org. Electronics* 11, 57 (2010).

[5] P. Zacharias, M. C. Gather, A. Köhnen, N. Rehm, K. Meerholz, *Angew. Chem. Int Ed.* 48, 4038 (2009).

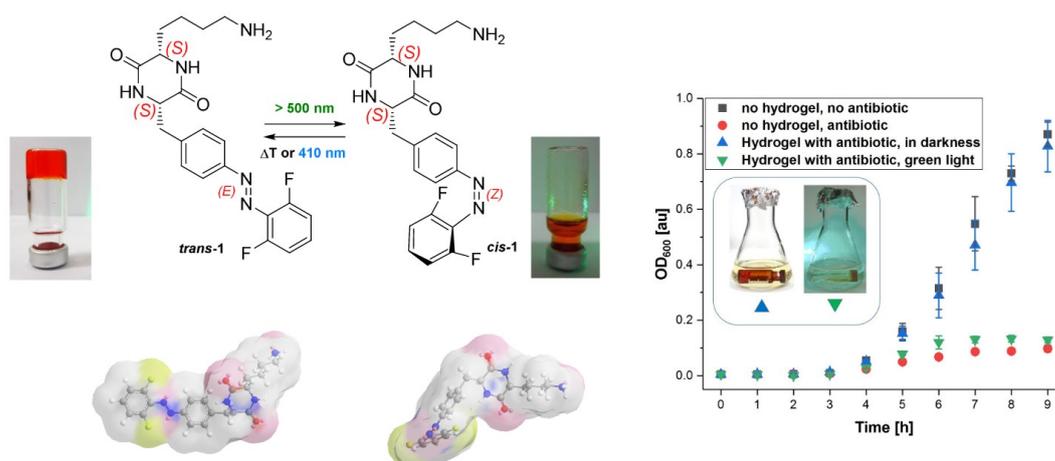
[6] R.C. Shallcross, P.O. Körner, E. Maibach, A. Köhnen, K. Meerholz, *Adv. Mat.* 34, 4807 (2013).

Photochromic peptides for visible-light-triggered hydrogels and beyond

Dr. Zbigniew Pianowski

IOC, KIT Karlsruhe, Fritz-Haber-Weg 6, 76131 Karlsruhe

Photoresponsive smart materials transform light energy into sophisticated functions.[1] They find increasing biomedical applications in light-induced drug release and photopharmacology, as they can locally provide the desired therapeutic effect due to precise spatiotemporal dosage control. However, the majority of reported studies rely on cytotoxic UV light that poorly penetrates tissues.[2] We have introduced a first photochromic low-MW supramolecular hydrogel that releases drugs under visible light irradiation.[3] This was achieved by coupling a previously developed low-molecular-weight hydrogelator with a fluorinated azobenzene motif switchable with green light.[4] The resulting hydrogels can encapsulate structurally unmodified drugs, as well as proteins. The cargo is efficiently released upon exposure on visible light. We demonstrated green-light-induced release of structurally unmodified antibiotic, anticancer, and anti-inflammatory drugs under physiological conditions. Using the antibiotic-loaded gel, we selectively inhibited bacterial growth with green light.



Upon investigation of potential guests for the hydrogel system, we have discovered peptoids of light-dependent cytotoxicity.[5] Our recent progress in the area of visible light-triggered hydrogels and photopharmacology will be presented.

References:

- [1] Z. Pianowski *Chem. Eur. J.* **2019**, *25*, 5128-5144.
- [2] I. Tomatsu, L. Peng, A. Kross. *Adv. Drug Delivery Rev.* **2011**, *63*, 1257.
- [3] J. Karcher, Z. Pianowski, *Chem. Eur. J.* **2018**, *24*, 11605-11610
- [4] D. Bleger, et al. *J. Am. Chem. Soc.* **2012**, *134*, 20597.
- [5] Z. Pianowski et al. "Diketopiperazine mit licht-aktivierter Zytotoxizität" Patent application (DPMA) priority date 12.07.2019

Light-controlled interactions of fluorophore-DAE conjugates linked to titanium dioxide surfaces

Karola Rück-Braun

Department of Chemistry, Technische Universität Berlin, Str. des 17. Juni 135, 10623 Berlin, Germany, Tel: +49-30-314-26319; E-mail:Karola.Rueck-Braun@tu-berlin.de

In the past years, we designed a series of BODIPY-DAE compounds with carboxylic acid anchoring groups, for reversible light modulation of electron- and energy transfer processes on titanium dioxide surfaces.¹⁻³ My talk will present almost pure two-state (OF and CF) investigations, because of nearly quantitative photoisomerization of the new fluorophore-DAE compounds, under UV- and visible light illumination,^{2,3} opposite to previously studied compounds from our group with other DAE substitution patterns and linker designs.³

1. F. Schweighoefer et al., Ultrafast dynamics of differently aligned COOH-DTE-BODIPY conjugates linked to the surface of titanium dioxide, *J. Phys.: Condens. Matter*, **2018**, *30*, 054001 (7pp).

2. N. Ziebart, et al., Synthesis and characterization of non-symmetrical photoswitchable DTE(OMe) sensitizers, *Tetrahedron*, **2018**, *74*, 5561-5566.

3. N. Ziebart, et al., A photochromic benzothiadiazole-diarylethene system with tunable On/Off fluorescence modulation, *ChemPhotoChem*, **2019**, *3*, 396-402.

Fluorescence microscopy with sub-molecular resolution with STM

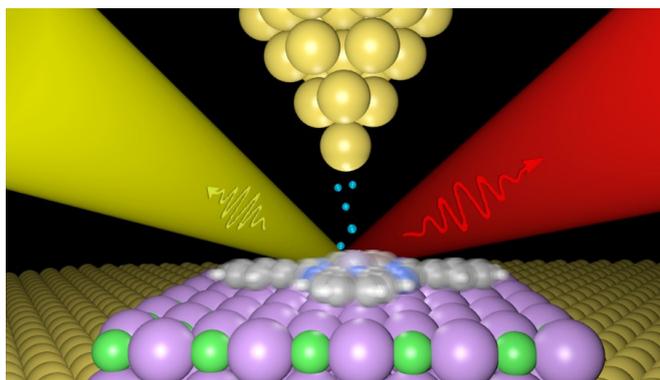
Guillaume Schull

Université de Strasbourg, CNRS, IPCMS, UMR 7504, F-67000 Strasbourg, France, schull@unistra.fr

The electric current traversing the junction of a scanning tunneling microscope (STM) may generate a local emission of light. During the last years, we have used this method to study the intrinsic luminescence properties of individual molecules. This work has progressed in two directions. On one side we have used the ability of the STM to manipulate matter with atomic-scale precision to form single-molecule light emitting devices whose color, intensity and bandwidth can be controlled with high precision [1,2,3].

On the other side, we used the STM to generate sub-molecularly resolved fluorescence maps of molecules separated from a metallic surface by a thin insulating layers. Combined with spectral selection and time-correlated measurements, this hyper-resolved fluorescence microscopy approach allowed us to scrutinize the vibronic structure of individual molecule [4], to characterize the photonics properties of charged species [5] and to track the motion of hydrogen atoms within free-based phthalocyanine molecules [6].

Together with other recent reports [7,8], this result constitutes an important step towards photonic measurements with atoms-scale resolution.



Artistic view of a single ZnPc molecule excited with STM

- [1] G. Reecht et al., Phys. Rev. Lett. 112, 047403 (2014)
- [2] M.C. Chong et al., Phys. Rev. Lett. 116, 036802 (2016)
- [3] M.C. Chong et al., Nanoletters 16, 6480 (2016)
- [4] B. Doppagne et al., Phys. Rev. Lett. 118, 127401 (2017)
- [5] B. Doppagne et al. Science, 361, 251 (2018)
- [6] B. Doppagne et al. unpublished
- [7] Y. Zhang et al. Nature 531, 623 (2016)
- [8] H. Imada et al., Nature 538, 364 (2016)

Implementing, Characterizing, and Utilizing Molecular Switches: The SURMOF Approach

Christof Wöll

Institute of Functional Interfaces (IFG), Karlsruhe Institute of Technology, North Campus, 76021 Karlsruhe

Realizing molecular “Designer Solids” by programmed assembly of building units taken from libraries is a very appealing objective. Recently, metal-organic frameworks (MOFs) have attracted a huge interest in this context. Here, we will focus on the integration of molecular switches into MOFs, as well as on several applications based on these highly versatile crystalline materials. For numerous MOF-based applications the conventional solvothermal synthesis yielding powders is not well suited, e.g. in optics the powder particles cause strong scattering which makes a reliable determination of photophysical parameters difficult. To overcome these problems, we have developed a layer-by-layer (lbl) deposition method to produce well-defined, highly oriented and monolithic MOF thin films on a number of different substrates. The resulting films are referred to as SURMOFs [1,2]. The fabrication of hetero-multilayers (see Fig. 1) is rather straightforward with this lbl method. In this talk, we will describe the principles of SURMOF fabrication as well as the results of systematic investigations of electrical and photophysical properties exhibited by empty MOFs and after loading their pores with functional guests. Subsequently we will focus on the implementation of molecular switches into SURMOFs, and the application for a variety of purposes.

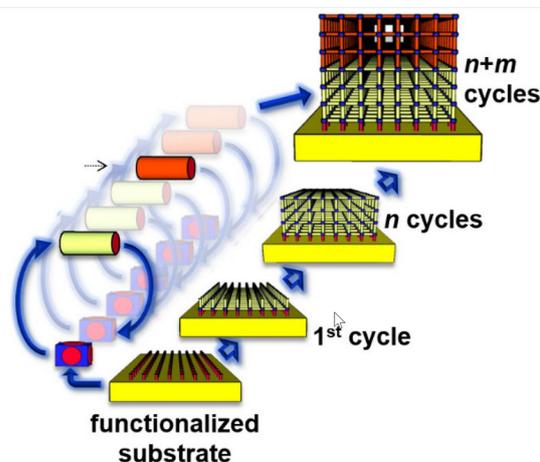


Fig. 1 Layer-by-layer scheme to fabricate SURMOFs

References:

- [1] J. Liu, Ch. Wöll, Chem. Soc. Rev. 46, 5730-5770 (2017)
- [2] L. Heinke, Ch. Wöll, Advanced Materials 31 (26), 1970184 (2019)

Functional molecular tripods

Wulf Wulfhekel

Physikalisches Institut, KIT Karlsruhe, wulf.wulfhekel@kit.edu

Molecules composed of a tripodal sulfur-anchored stand in combination with a functional group allow to firmly anchor the molecule in a defined adsorption geometry on Au(111) surfaces lifting the functional group from the surface into the vacuum for observation with the tip of a scanning tunneling molecule. We will summarize our activities on this concept including: (i) molecular cantilevers with functional groups containing electric dipole moments for the realization of molecular switches driven by the electric field in the tunneling junction [1], (ii) molecular motors, in which a freely rotatable functional group can be switched between several states by the action of the tunneling electrons [2], and (iii) preliminary results on electroluminescence from chromophores in the functional group to insulate them from the substrate and to decrease the non-radiative recombination rate. We will discuss advantages and problems of this approach as well as a perspective.

[1] Lukas Gerhard et al., *Nature Comm.* 8, 14672 (2016).

[2] Jan Homberg et al., *Nanoscale* 11, 9015 (2019).

ABSTRACTS FOR INTERNAL SFB 677 LECTURES

in order of project ID

Project A01: Ultrafast Dynamics of Photo-induced Switching Processes

Friedrich Temps, [Falk Renth](#), Bernd Hartke

Institute of Physical Chemistry, CAU Kiel

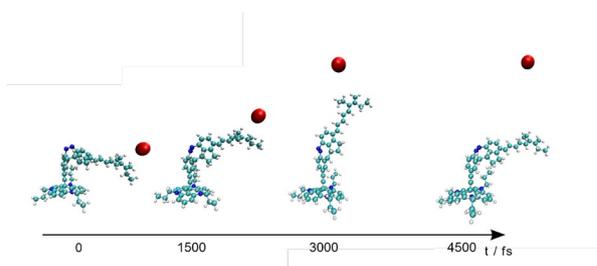
In project A1, experimental ultrafast spectroscopy and theoretical chemistry collaborate to investigate fundamental photo-induced processes of molecular switches, ranging from isolated switchable molecules and molecular assemblies of several chromophores all the way to molecular photoswitches acting in complex environments. The numerous highlights of this project include the following:

Optimized diazocine switches: In the 1st phase of CRC 677, diazocine was recognized as an improved variant of the frequently used azobenzene. Our theoretical photodynamics simulations indicated that flexibilizing the additional C-C bridge in diazocine, e.g., by inserting an oxygen atom into it, would lead to further improvements. The superior photophysical properties of a new oxa-diazocine switch and the pivotal role of a second, chair-like ground-state conformer were confirmed experimentally and serve as successful example for the rational improvement of photoswitchable systems.

Excited-state energy transfer (EET) in photoswitchable systems: The feasibility of sensitized photoswitching by photo-induced EET was studied in a model dyad consisting of a benzimidazole donor fluorophore linked to a photoswitchable naphthopyran acceptor. Our results indicated a fast (2.9 ps), practically quantitative EET from the donor-excited to the acceptor-excited state, which could be modeled successfully by Förster resonance energy transfer (FRET) and resulted in the desired ring opening of the naphthopyran. The obtained insight should aid in the development of devices utilizing FRET for sensitized photoswitching. In another line of research, the UV-initiated ultrafast photodynamics of a photoswitchable spin-crossover iron(II) complex with a photoisomerizable ligand was studied. Here, the desired photoisomerisation of the ligand turned out to be quenched due to a competing ultrafast EET to a metal-to-ligand charge-transfer (MLCT) state. To create magnetically bistable systems via this approach, photochromic ligands switchable at wavelengths to the red of the MLCT bands, or metal-ligand systems without MLCT transitions in the UV/Vis region should be used.

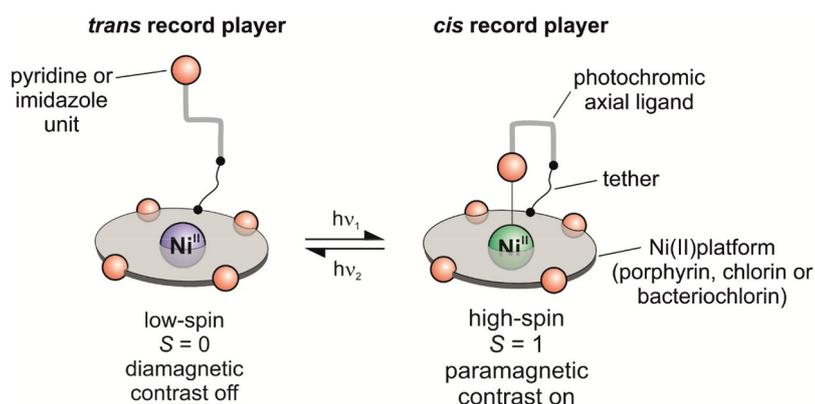
Photoswitching in poly(azobenzene-trisiloxane): The ultrafast photo-induced processes of a poly(azobenzene-trisiloxane) with azobenzenes as photoswitchable units in the main chain connected by trisiloxane linkers were studied in detail. The results suggest that the isomerisation of the main-chain azobenzene units occurs essentially unhindered via reaction pathways conforming to the accepted scenario for azobenzene in solution. This explains the observed unusually efficient and reversible photoisomerisation of the main-chain poly(azobenzene-trisiloxane), and emphasizes its potential as a new photo-responsive material with high switching amplitude.

Transport by photoswitchable molecular cilia: From the inception of CRC 677, a guiding vision was to create artificial cilia with photoswitchable molecular motors, attached to a surface via TATA platforms (project B9), and to use them as drivers of particle transport at the nanoscale. With our theoretical simulations, we could contribute to understanding how TATA platforms form regular adlayers on surfaces and we could demonstrate actual transport, with QM/MM simulations of a full cilium setup (TATA platform, diazocine motor, tail, transport target).



Project A06: Switchable Contrast Agents for Magnetic Resonance ImagingVanessa Wellm,^a Jannis Ludwig,^a Marcel Dommaschk,^b Gernot Heitmann,^c Jens Groebner,^d Rainer Herges^a^a Otto Diels Institute of Organic Chemistry, Otto-Hahn-Platz 4, 24118 Kiel, Germany^b School of Chemistry, University of Manchester, Manchester M13 9PL, UK^c IWS Innovations- und Wissensstrategien GmbH, Aviares, Aviation Research Network, Deichstraße 25, 20459 Hamburg, Germany^d South Westphalian University of Applied Sciences, Department for Electrical Engineering and Information Technology, Haldener Straße 182, 58095 Hagen, Germany

Ni(II)porphyrins can be switched between a diamagnetic and paramagnetic state at room temperature by light-driven coordination-induced spin state switch (LD-CISSS). Switching of the coordination number and subsequently of the spin state is achieved by using Ni(II)porphyrin as a square planar platform and azopyridine or azoimidazole as a photoswitchable axial ligand that is bonded covalently at one *meso* position of the porphyrin. The square planar Ni(II)porphyrin of the so called record player molecule is diamagnetic (low-spin, $S = 0$) while the square pyramidal complex is paramagnetic (high-spin, $S = 1$). The switching process can be controlled by irradiation with light of different wavelengths. The photoswitchable azopyridine only binds in the *cis* configuration and dissociates in the *trans* form. This LD-CISSS is a novel approach for the design of light responsive MRI contrast agents (scheme 1).^[1-5]



Scheme 1. Reversible light-induced magnetic switching of a photochromic ligand functionalized Ni(II)porphyrin.

In the last funding period we were focused on solving a number of problems prior to applications *in vivo*:

1. introducing water solubility, switching in water and human serum^[5,6]
2. shifting the wavelengths of the switching process to the bio optical window (650- 850 nm)^[6,7]
3. synthesis of smart contrast agents that are sensitive to physiological parameters (temperature, pH)^[6,8,9]
4. developing MR sequences for determination of relaxation times as well as the measurement of switching kinetics with high temporal and spatial resolution^[10]

Literature:

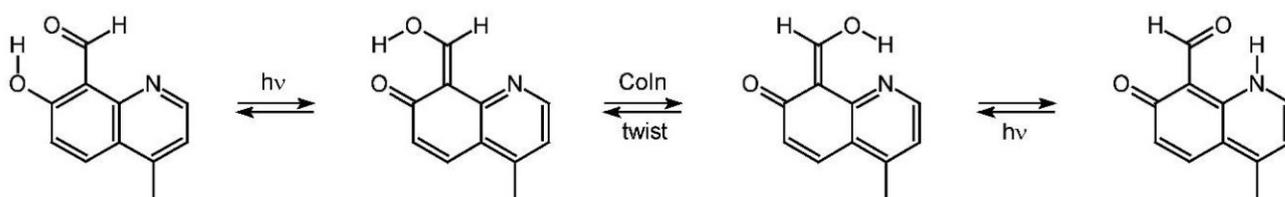
[1] S. Thies et al., *J. Am. Chem. Soc.* **2011**, *133*, 16243-16250; [2] S. Venkataramani et al., *Science* **2011**, *331*, 445-448; [3] S. Thies et al., *Chem. Eur. J.* **2012**, *18*, 16358-16368.; [4] M. Dommaschk et al., *J. Am. Chem. Soc.* **2015**, *137*, 7552-7555; [5] M. Dommaschk *Dissertation*, CAUKiel **2016**; [6] V. Wellm, *current work*, CAUKiel **2019**; [7] M. Dommaschk, V. Thoms et al., *Inorg. Chem.* **2015**, *54*, 9390-9392; [8] G. Heitmann, *unpublished results*, CAU Kiel **2016**; [9] J. Ludwig, *current work*, CAU Kiel **2019**; [10] J. Groebner, *current work*, CAU Kiel **2019**.

Project A07: Dynamics of Intramolecular H-Transfer Photoswitches

Bernd Hartke,^{a)} Ulrich Lüning,^{b)} Friedrich Temps^{a)}

a) Institute of Physical Chemistry; b) Otto-Diels-Institut für Organische Chemie, CAU Kiel

Photochromic molecular switches based on excited-state intramolecular proton transfer (ESIPT) belong to the fastest chemical processes known. Hence, competing side reactions are virtually impossible and exceptional photostabilities can be reached. Based on quasi-static theoretical calculations, Sobolewski et al. [Phys. Chem. Chem. Phys. 2008, 10, 1243] proposed a new combination of ESIPT processes with intermediate, torsional motion of a “crane” group. The net result of the desired ESIPT-crane-ESIPT steps is a medium-range transport of the proton along the molecular scaffold:



In Project A7, we investigate the photo-induced molecular mechanisms and dynamics of such prototypical photochromic switches that combine ESIPT and crane features, by joining forces from Physical Chemistry (femtosecond spectroscopy), Organic Chemistry (synthesis), and Theoretical Chemistry (quantum-chemical molecular dynamics calculations).

A rational molecular design of such systems calls for a variety of cranes and of proton donor and acceptor groups, and for ensuring solubility in solvents that do not interfere with ESIPT and with infrared (IR) spectroscopy. Accordingly, we successfully synthesized a broad palette of such variations. Theoretical simulations initially focused on smaller model systems to verify the employed methods and to investigate the basic mechanistic steps. Using a well-established direct dynamics approach with semiempirical configuration-interaction, however, we could also demonstrate already that the full ESIPT-crane-ESIPT sequence shown above is in fact happening in this very system. Using femtosecond UV-vis transient electronic absorption spectroscopy (TEAS), clear indications for ultrafast processes in several of these new ESIPT/crane systems could be obtained.

Beyond the above hydroxyquinoline-derived systems with different proton donor, acceptor and crane stations, we successfully established sequential excited-state proton transfer mechanisms in N-(3-pyridinyl)-2-pyridine-carboxamide (N3PPCA) and N-(2-pyridinyl)-2-pyridine-carboxamide (N2PPCA) by means of transient vibrational absorption spectroscopy (TVAS). Compared to the usually broad and structureless electronic absorption bands seen by TEAS, TVAS offers the advantage of chemical specificity. The observed vibrational features are usually assignable with help from quantum chemical calculations. N3PPCA showcases a fifth and a sixth proton transfer station compared to N2PPCA. Last but not least, new TVAS results have shown intermolecular excited-state proton and double-proton transfer in H-bonded 2-aminopurine-thymine base pairs in Watson-Crick- and Hoogsteen conformations.

Project A08: Light-driven molecular Assemblers for the artificial Oxoanion condensation

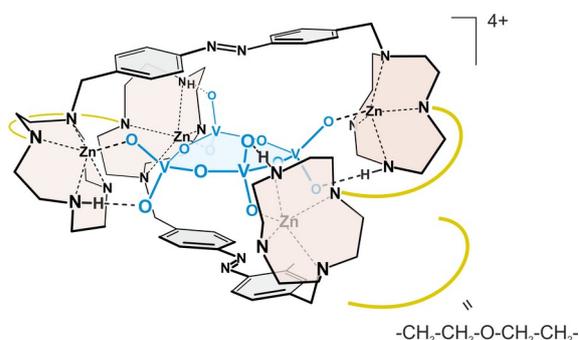
Daniel Hugenbusch, Fabian Kruse and Rainer Herges

Otto Diels Institute for Organic Chemistry, Christian-Albrechts-University, Kiel, 24118 Germany, Tel: +49-431-8801929; E-mail: dhugenbusch@oc.uni-kiel.de, fkruse@oc.uni-kiel.de, rherges@oc.uni-kiel.de

Inspired by the process of photosynthesis, we are aiming at the design, synthesis and investigation of a model system of molecular assemblers.

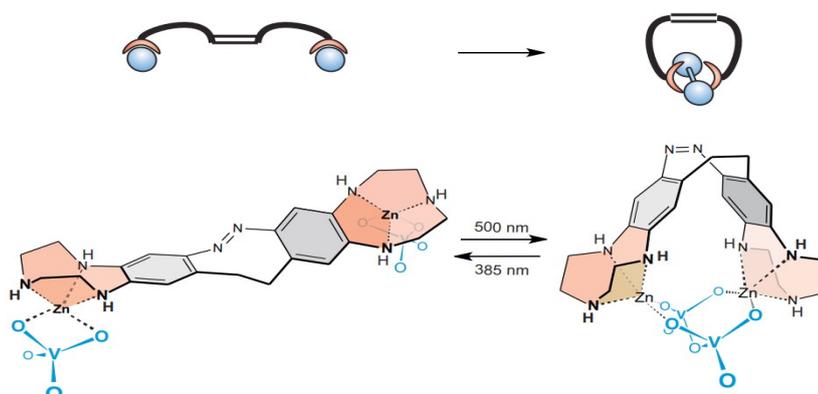
In preliminary work in our research group a light-switchable ditopic receptor was synthesized, which is able to drive the condensation of 4 molecules of monovanadate to a cyclic tetravanadate.^[1] This receptor contains two zinc-cyclene units as binding sites for oxoanions and a photoswitchable azobenzene unit.

In order to improve the binding of tetravanadate, two of these receptor molecules are connected via spacer units to form a cage-like structure. Suitable spacers are determined by quantum mechanical calculations. Two diethyl ether linkers for example permit an energetically favorable complexation.



Another class of receptor molecules includes diazocines as photoswitches to achieve a pincer-like motion, reduce the degrees of freedom and improve the force transmission.

Moreover diazocines exhibit superior photoswitching properties compared to azobenzene.^[2] Furthermore the coordination units for oxoanions are varied.

**References**

- [1] H. Sell, A. Gehl, D. Plaul, F. D. Sönnichsen, C. Schütt, F. Köhler, K. Steinborn, R. Herges, *Commun. Chem.* **2019**, *2*, 1-6.
 [2] R. Siewertsen, H. Neumann, B. Buchheim-Stehn, R. Herges, C. Näther, F. Renth, R. Temps, *J. Am. Chem. Soc.* **2009**, *131*, 43, 15594-15595.

Project B07: Switching the spin of single molecules on surfaces

Manuel Gruber, Richard Berndt

Institut für Experimentelle und Angewandte Physik, Christian-Albrechts-Universität zu Kiel, 24098 Kiel

Molecular electronics aims at utilizing functional molecules as building blocks of electronic components. In that respect, molecules adsorbed on a surface exhibiting spin switching functionality are particularly interesting. Molecules possessing different properties were deposited on metallic surfaces using two different techniques: sublimation for the most robust molecules and electrospray deposition for the more fragile molecules. The adsorption, along with the electronic and magnetic properties of the deposited molecules, were investigated using low-temperature scanning tunneling microscopy and spectroscopy along with x-ray absorption spectroscopy. The molecules were switched using different triggers, e.g., electrons, coordination of axial ligands, contact with the STM tip. This results in various changes of the molecular properties such as their adsorption properties [1] and their electronic and magnetic properties [2-4]. A strong emphasis will be given on the investigation of so-called hairclip complexes, a new class of molecules where coordination and spin switching are interlocked [5]. Furthermore, it will be shown that magnetism can be induced and controlled in non-magnetic molecule through controlled supramolecular manipulations [6].

References:

[1] **A surface ciseffect: Influence of an axial ligand on molecular self-assembly.**

Th. Knaak, T. G. Gopakumar, B. Schwager, F. Tuczek, R. Robles, N. Lorente, R. Berndt, *J. Am. Chem. Soc.* **2016**, *138*, 7544–7550.

[2] **Deposition of a cationic Fe(III) spin-crossover complex on Au(111): Impact of the counter ion.**

T. Jasper-Tönnies, M. Gruber, S. Karan, H. Jacob, F. Tuczek, R. Berndt, *J. Phys. Chem. Lett.* **2017**, *8*, 1569–1573.

[3] **Robust and selective switching of a Fe(III) spin-crossover compound on Cu₂N/Cu(100) with memristance behavior.**

T. Jasper-Tönnies, M. Gruber, S. Karan, H. Jacob, F. Tuczek, R. Berndt, *Nano Lett.* **2017**, *17*, 6613–6619.

[4] **Spin control induced by molecular charging in a transport junction.**

S. Karan, C. Garcia, M. Karolak, D. Jacob, N. Lorente, R. Berndt, *Nano Lett.* **2018**, *18*, 88–93.

[5] **Reversible coordination-induced spin-state switching in complexes on metal surfaces.**

A. Köbke, F. Gutzeit, F. Roehricht, R. Herges, A. Schlimm, J. Grunwald, F. Tuczek, M. Studniarek, F. Choueikani, E. Otero, P. Ohresser, S. Rohlf, S. Johannsen, F. Diekmann, K. Rossnagel, T. Jasper-Tönnies, C. Näther, R. Herges, R. Berndt, M. Gruber, submitted.

[6] **Inducing and controlling molecular magnetism through supramolecular manipulation.**

J. Homberg, M. Gruber, A. Weismann, R. Berndt, in preparation.

Project B10: First-principles study of tip-adsorbate interactions in scanning probe experiments

Stefan Heinze

Institut für Theoretische Physik und Astrophysik, Leibnizstr. 15, 24098 Kiel, heinze@physik.uni-kiel.de

Scanning tunneling microscopy (STM) is a key experimental technique to address individual molecules on surfaces and to probe their structural, electronic, and magnetic properties. It is even possible to switch a molecular state by applying current pulses, electric fields, or by direct interaction with the STM tip. The forces between molecule and tip can be measured by atomic force microscopy (AFM). Microscopes which combine both STM and AFM allow to measure conductance and force curves simultaneously. With magnetic tips this technique can be made spin sensitive allowing to measure both spin-polarized currents and exchange forces as recently demonstrated [1]. However, the interpretation of such experiments is often non-trivial and first-principles calculations based on density functional theory (DFT) have become an indispensable theoretical tool.

Here, I will show how we can understand the tip-molecule interaction and the conductance in STM/AFM measurements on SnPc molecules on a Ag(111) surface [2] based on DFT. The conductance as a function of tip-molecule separation exhibits an exponential dependence with similar decay length for the two possible configurations. However, the short-range forces between tip and molecule display a non-trivial distance dependence distinctively different from those of single-atom contacts as shown by DFT. Therefore, molecule deformations occur which lead to the unexpected force curves. Quantitative spin-sensitive STM/AFM measurements have recently been performed for a Mn monolayer on W(110) [3] which exhibits a cycloidal spin spiral. This surface is ideally suited to study single magnetic atoms or molecules as their spin quantization axis can be rotated quasi continuously by exchange coupling to the spin spiral [4-6]. Our DFT calculations reveal that the measured atomic-scale variations in the exchange force on Mn/W(110) originate from different contributions of direct and indirect exchange mechanisms depending on the chemical tip termination [3].

[1] N. Hauptmann, J. Gerritsen, D. Wegner, and A. A. Khajetoorians, *Nano Lett.* **17**, 5660 (2017).

[2] N.M. Caffrey, K. Buchmann, N. Hauptmann, C. Lazo, P. Ferriani, S. Heinze and R. Berndt, *Nano Lett.* **15**, 5156 (2015).

[3] N. Hauptmann, S. Haldar, T.-C. Hung, W. Jolie, M. Gutzeit, D. Wegner, S. Heinze, and A. A. Khajetoorians, in preparation.

[4] D. Serrate, P. Ferriani, Y. Yoshida, S.-W. Hla, M. Menzel, K. von Bergmann, S. Heinze, A. Kubetzka, and R. Wiesendanger, *Nat. Nanotechnol.* **5**, 350 (2010).

[5] N. M. Caffrey, P. Ferriani, S. Marocchi, and S. Heinze, *Phys. Rev. B* **88**, 155403 (2013).

[6] S. Haldar and S. Heinze, *Phys. Rev. B* **98**, 220401 (R) (2018).

Project B11: Sweet Switches

Thisbe K. Lindhorst

Otto Diels Institute for Organic Chemistry, Otto-Hahn-Platz 3, 24118 Kiel, tkind@oc.uni-kiel.de

All cells are covered by a sweet molecular layer of particular complexity, dimension and biological significance. This extracellular compartment is called a cell's glycocalyx. Molecular recognition of glycocalyx constituents such as glycoconjugates and their interaction with specialized proteins are fundamental to cell biology. An important part in the orchestration of carbohydrate recognition on the cell surface is apparently played by relative orientation of sugar epitopes. In order to investigate the relevance of sugar orientation, we have started a program involving sugars & light, to switch carbohydrate orientation on surfaces, such as for the control of bacterial adhesion. We have additionally commenced a project dedicated to the synthesis and testing of "pseudoenantiomeric glycoclusters" to investigate the significance of carbohydrate orientation in carbohydrate recognition. For the biological evaluation we are employing the mannose-specific adhesion of type 1-fimbriated *Escherichia coli*.

Project B12: Control of Surface Plasmon Polariton Propagation by Molecular Switches

Michael Bauer

Institut für Experimentelle und Angewandte Physik, Universität Kiel, Leibnizstr. 19, 24118 Kiel, Germany

In the recent past different schemes for the realization of active plasmonics, i.e., the external control of the response of plasmonic systems, have been introduced using for instance interactions mediated by quantum dots [1] or nonlinear interactions with intense light pulses [2]. In a work by Pala et al. it was demonstrated that also photochromic molecules can be used as active control units for plasmonic excitations [3]. Photochromic molecules guarantee the non-volatility in the switching behavior, which is an important advantage with respect to potential applications in comparison to many other approaches.

In this talk I will present results on the control of surface plasmon polaritons (SPP) using photochromic molecules that we achieved within the third funding period of the SFB. Using photoemission electron microscopy (PEEM) and surface plasmon resonance spectroscopy we are able to experimentally demonstrate and quantify the reversible switching of SPP propagation using spiropheanthrooxazine (SPO) molecules (see Fig. 1). Implementation into a SPP lens shows furthermore how this concept can be used for the operation of a plasmonic device [4]. Finally I will present our first attempts toward the realization of switchable plasmonic waveguides [5] and discuss prospects how to improve in the future the switching contrast of the plasmonic response.

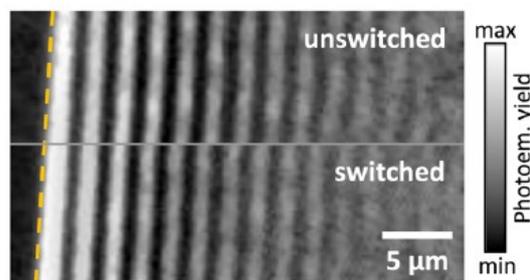


Fig. 1. PEEM images of a SPP intensity pattern mapped before (unswitched) and after (switched) illumination of a switchable SPP supporting interface with UV light ($\lambda = 365$ nm); the change in the periodicity of the pattern is indicative of a change in the real part of the SPP wave vector. Figure taken from Ref. [3].

- [1] P. Vasa, W. Wang, R. Pomraenke, M. Lammers, M. Maiuri, C. Manzoni, G. Cerullo, C. Lienau, *Nature Photon.* 2013, 7, 128.
- [2] K. F. MacDonald, Z. L. Sámson, M. I. Stockman, N. I. Zheludev, *Nature Photon.* 2009, 3, 58.
- [3] R. A. Pala, K. T. Shimizu, N. A. Melosh, M. L. Brongersma, *Nano Lett.* 2008, 8, 1506.
- [4] M. Großmann, A. Klick, C. Lemke, J. Falke, M. Black, J. Fiutowski, A. Goszczak, E. Sobolewska, A. Usman Zillohu, M. Keshavarz Hedayati, H.-G. Rubahn, F. Faupel, M. Elbahri, M. Bauer, *ACS Photonics* 2015, 2, 1327
- [5] M. Großmann, M. Thomaschewski, A. Klick, A. J. Goszczak, E. K. Sobolewska, T. Leifßner, J. Adam, J. Fiutowski, H.-G. Rubahn, M. Bauer, *Plasmonics* 2018, 13, 1441.

Project C12: Photoswitchable Protein Kinase Inhibitors for Novel Anti-Cancer Applications

Dorian Schmidt¹, Miriam Schehr², Julia Ewert², Linda Heintze¹, Theo Rodat¹, Rainer Herges², Christian Peifer^{1,*}

1: Institute of Pharmacy, University of Kiel; Gutenbergstr. 76, 24118 Kiel, Germany;

2: Institute of Organic Chemistry, University of Kiel, Otto-Hahn-Platz 4, 24098 Kiel, Germany;

email: dschmidt@pharmazie.uni-kiel.de

Protein kinases are enzymes that mediate signal transduction in intracellular signal pathways and regulate cell growth and differentiation. Overactivated kinases, however, can lead to uncontrolled cell proliferation and play a crucial role in tumor progression and inflammatory diseases. Therefore, kinases are important drug targets and the development of small molecule kinase inhibitors has become a major field in pharmaceutical research.^[1]

In this project, we have developed photoswitchable small molecule kinase inhibitors that can be switched between a bio-active and a bio-inactive configuration by light.

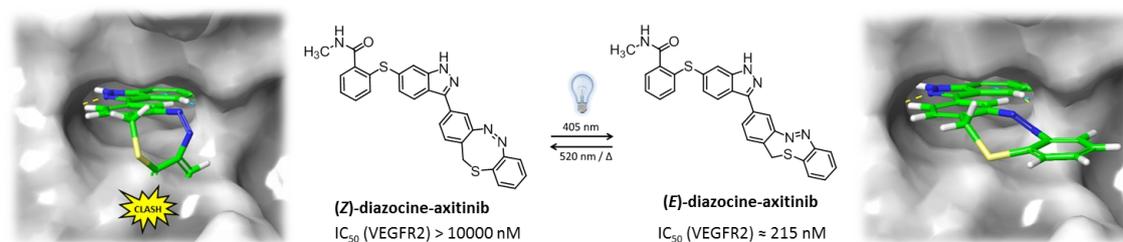


Figure 1. (Left): Superposition of (*Z*)-diazocine-axitinib (green tube representation) with the ATP binding pocket of VEGFR2 (pdb code 4AG8).^[2] In the *Z*-configuration the diazocine moiety clashes with the protein surface (gray). No binding mode can be found by molecular modeling. (Middle): *E/Z*-isomerization of diazocine-axitinib. (Right): Calculated binding mode of (*E*)-diazocine-axitinib with VEGFR2.

As a start, we investigated the photo-induced *E/Z*-isomerization of the approved kinase inhibitor axitinib that possesses a stilbene-like moiety by chance. We could demonstrate that (*E*)-axitinib can be activated *in vitro* almost quantitatively by irradiation with light of 385 nm. However, photoswitching of axitinib in aqueous solutions is irreversible due to a competing [2+2]-cycloaddition.^[3]

To obtain reversibly switchable inhibitors, we have synthesized a suite of diazocine-functionalized axitinib derivatives (Figure 1). In the thermodynamically stable *Z*-configuration these compounds do not show activity in an *in vitro* VEGFR2 kinase assay ($IC_{50} > 10000$ nM). However, by irradiation with light (405 nm) the activity can be significantly increased resulting in an IC_{50} value of 215 nM. The *E*-isomer can be switched back to the bio-inactive *Z*-isomer either with visible light (520 nm) or thermally ($t_{1/2} \approx 6.6$ h at 37 °C).

We also applied the photoswitchable inhibitor approach to other classes of kinases including CK1 δ and BRAF^{V600E}.^[4,5] As photoswitches we used both, classical azobenzenes as well as diazocines.

References

1. J. Zhang, P. L. Yang, N. S. Gray, Nat. Rev. Cancer 2009, 9, 28-39.
2. M. McTigue et al., Proc. Natl. Acad. Sci. U.S.A. 2012, 109, 18281-18289.
3. D. Schmidt, T. Rodat et al., ChemMedChem 2018, 13, 2349-2463.
4. M. Schehr, Photochem. Photobiol. Sci. 2019, 18, 1398-1407.
5. M. Hoorens, Eur. J. Med. Chem. 2019, 179, 133-146.

Project C13: X-Ray Reflectivity Investigation of Structure and Kinetics of Photoswitchable Lipid Monolayers

Jonas Warias¹, Franziska Reise², Svenja Hövelmann¹, Rajendra Giri¹, Andrea Sartori¹, Sven Festersen¹, Olaf Magnussen¹, Thisbe Lindhorst², Bridget Murphy¹

1 Institute of Experimental and Applied Physics, Leibnitzstrasse 11-19, 24118 Kiel, Germany

2 Otto Diels Institute of Organic Chemistry, Otto-Hahn-Platz 3-4, 24118 Kiel, Germany

The mechanical and dynamic properties of phospholipid membranes are of importance for biological functions, such as switching of embedded proteins and cell transport. In order to investigate these properties we study model systems in which amphiphilic photoswitchable molecules are integrated into Langmuir films of phospholipids. We have modified glycolipids to contain an azobenzene photoswitch between the chain and the head group and successfully embedded those in a monolayer of dipalmitoylphosphatidylcholine (DPPC)[1]. This allows us to reversibly change the azobenzene-glycolipid orientation between trans- and cis-conformation by illumination with UV and blue light. We investigated the switching behavior with Langmuir isotherms and observed an additional phase transition compared to DPPC monolayer. Additionally we have followed the structural changes in this model membrane and the switching kinetics of the system with in situ X-ray reflectivity and Grating Incident Diffraction at the LISA diffractometer P08, PETRA III[2]. Strong changes in membrane conformation upon switching have been observed.

[1] F. Reise et al., Chem. Eur. J. 17497-17505 (2018)

[2] B. M. Murphy et al., J. Syn. Rad. 45-56 (2014) 21

ABSTRACTS FOR POSTERS

in alphabetical order of presenters

A novel approach for fabrication of photochromic organic thin films via Initiated Chemical Vapor Deposition (iCVD)

Maximilian Heiko Burk, Faculty of Engineering, Kaiserstr. 2, 24098 Kiel

Initiated chemical vapor deposition (iCVD) is a solvent-free, cost efficient technique to synthesize highly conformal organic thin films from the vapor phase. The underlying free radical polymerization can be specifically tuned by the deposition parameters and enables furthermore copolymerization from various comonomer feed, enabling a wide field of applications like surface functionalization, biomedical applications and optical devices. [1] In this work we demonstrate the first ever synthesis of photochromic organic thin films via iCVD-deposition. The underlying concept is represented by sublimation of a solid photoswitchable Styrenediazocine in a tailor-made steel-unit, and transportation into the reactor-chamber via an inert carrier-gas. The photochromic compound was co-polymerized with V3D3, a triple-functional cyclic compound to guarantee maximum rotational-freedom of the azo-group after covalent-bonding. Due to a high controllability of the uniform film-formation, topography-preservation and manifold choice of potential substrates it is possible to equip surfaces with photoswitchable properties in the nano-range without losing the characteristic properties of the material. The chemical composition of the deposited films is decisive for their resulting properties. A detailed chemical characterization e.g. by X-ray photoelectron spectroscopy (XPS), Fourier-transform infrared spectroscopy (FTIR) and ellipsometry is thus inevitable for a deeper understanding of the resulting film properties. Functional groups and film composition can be tuned by the choice of precursors as well as the deposition parameters.

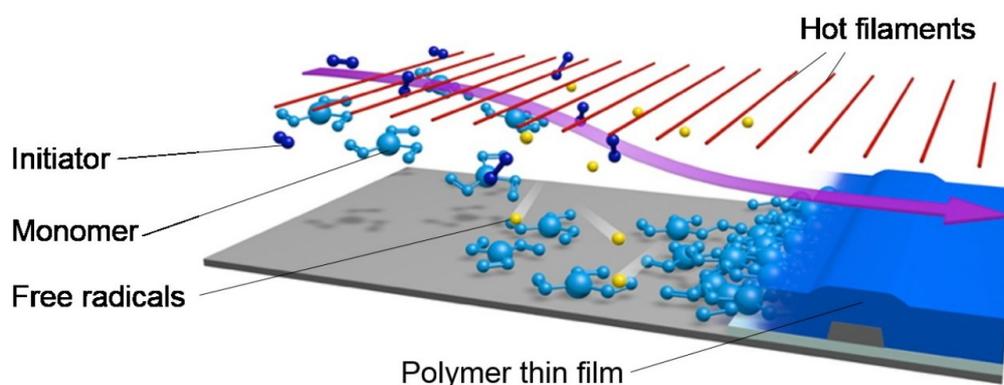


Fig 1: Schematic representation of the characteristic iCVD-reaction, where the precursors are activated by streaming through a hot filament plane. After adsorption of the reactive species on the substrate's surface, radical polymerization takes place.[2]

References

- [1] M. Wang, X. Wang, P. Moni, A. Liu, D. H. Kim, W. J. Jo, H. Sojoudi, K. K. Gleason *Advanced Materials* 29, 2017.
- [2] H. Moon et al., *Nature Materials* 14, 628-635, 2015.

Ecotoxicologically compatible drugs: Development of locally and temporally controlled pharmacophors

Julia Ewert

Otto Diels Institute for Organic Chemistry, Otto-Hahn-Platz 4, 24118 Kiel

Many conventional drugs have only a poor selectivity, show many side effects, encourage the emergence of resistance and have an environmental toxicity. These problems originate in uncontrolled drug activity in time and space. The approach of photopharmacology can be used for a selective limitation of the effective range of drugs. Excellent chromophores for this concept are diazocines. They can switch from their stable bioinactive *cis* isomer to the metastable bioactive *trans* isomer. The thermal reversion into the inactive state can be used for the design of environmentally friendly drugs. To combine the pharmaceutical function of drugs with ecological compatibility four different diazocine-based estrogen receptor modulators, which were designed by molecular modelling, were synthesized and photochemically characterized. The approach can be extended to many other environmentally relevant drugs therefore, a diazocine-based COX-2 inhibitor was developed.

Photoswitching of Azobenzene Glycoside Monolayers: Synthesis and Testing

Ellen Fast, Otto-Diels-Institut für Organische Chemie, Otto-Hahn-Platz 4, 24118 Kiel, efast@oc.uni-kiel.de

Glycocalyx, the carbohydrate-rich layer on the outer surface of eukaryotic cells, is one of the most important and intriguing surfaces in biology. Molecular interactions between the glycocalyx and the carbohydrate-specific proteins (lectins) initiate multiple biological functions such as cell adhesion, immune response, and cell signalling. Adhesion of bacterial cells to their host cells also occurs through the specific binding of adhesive organelles of bacteria, known as fimbriae with glycocalyx components present on the host cell surface. It has recently been shown that photoswitchable SAMs (self-assembled monolayers) of azobenzene glycosides on gold surface can be prepared.¹ With these SAMs it has been, for the first time, shown that three dimensional presentation of carbohydrates is critical in their interaction with bacteria.² The adhesion of bacteria with these glycosides was altered by photoswitching the azobenzene configuration. In the SAMs, the azobenzene moiety serves as a “hinge” that effects a defined change in carbohydrate orientation upon irradiation with light of a specific wavelength (Fig.1, left). Currently, we are trying to improve photoswitching on surfaces and to understand the structure-function relationships that underlie the observed biological effects. Photoisomerization of the azobenzene N=N double bond from the *E* into the *Z* state apparently requires empty space between the ligands on the surface. Therefore, we have initially effected *E*→*Z* isomerization on surface, using diluted SAMs (Fig.1, left).¹ In order to gain space between the switching molecules, instead of using diluter molecules, we installed a bulky protecting group, at the mannose headgroup (Fig. 1, middle), which is cleaved after SAM formation. In a second approach we synthesized biphenyl azobenzene glycosides with rigid backbones. It is reported in the literature, that SAMs made of bi- and terphenyl azobenzenes show excellent switching ability due to the dense packing and π - π

interactions.^{3,4} Hence, here we report the synthesis of the “self-diluting” mannoside **1**, biphenyl azobenzene glycosides **2-4** with rigid backbones, and the characterization and photoswitchability of the resulting glyco-SAMs via IRRAS (infrared reflection adsorption spectroscopy).

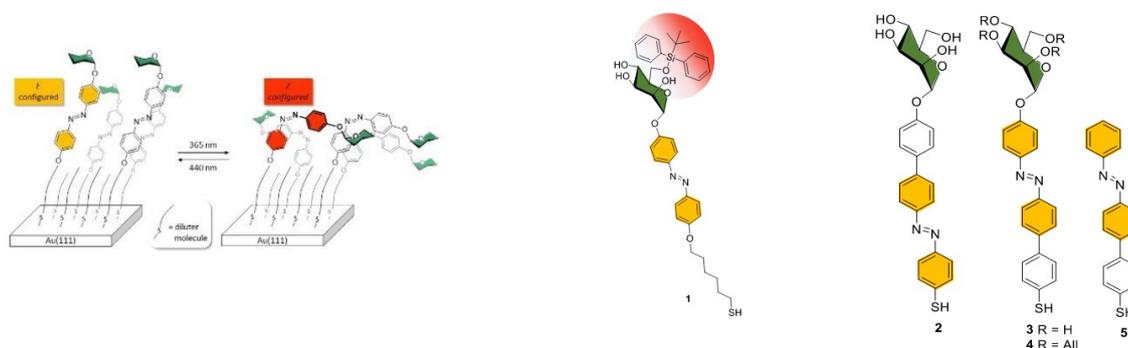


Figure 1: Photoswitchable azobenzene glycosides. Left: *E/Z* photoisomerization of diluted glyco-SAMs; middle: “self-diluting” mannoside **1**; right: mannosides with biphenyl azobenzene backbone **2-4** and diluter azobenzene **5**.

References:

[1] V. Chandrasekaran, H. Jacob, F. Petersen, K. Kathirvel, F. Tucek, Th. K. Lindhorst, *Chem. Eur. J.* **2014**, *20*, 8744-8752; [2] T. Weber, V. Chandrasekaran, I. Stamer, M. B. Thygesen, A. Terfort, Th. K. Lindhorst, *Angew. Chem. Int. Ed.* **2014**, *53*, 14583-14586; [3] V. Ferri, M. Elbing, G. Pace, M. D. Dickey, M. Zharnikov, P. Samori, M. Mayor, M. A. Rampi, *Angew. Chem. Int. Ed.* **2008**, *47*, 3455-3457; [4] N. Crivillers, A. Liscio, F. Di Stasio, C. Van Dyck, S. Osella, D. Cornil, S. Mian, G. M. Lazzarini, O. Fenwick, E. Orgiu, F. Reinders, S. Braun, M. Fahlman, M. Mayor, J. Cornil, V. Palermo, F. Cacialli, P. Samori, *Phys. Chem. Chem. Phys.* **2011**, *13*, 14302–14310.

Design and Synthesis of non-porphyrin based LD-CISSS Complexes for Switchable MRI Contrast Agents

Kim Daniela Fischer, Prof. Dr. Felix Tucek, Christian-Albrechts-Universität, Max-Eyth-Str. 2, 24118 Kiel/D

LD-CISSS (Light-Driven Coordination-Induced Spin State Switching) is one of the light-induced spin switching mechanisms.^[1] By isomerization of a photoswitchable ligand the coordination number of the metal ion changes which leads to a spin transition between the high spin state and the low spin state. In case of iron(II) switching between the low spin and the high spin complex implicates a change between diamagnetic and paramagnetic. Such LD-CISSS systems are suitable candidates for switchable contrast agents for MRI.^[2]

We developed tridentate iron(II) complexes to investigate the coordination-induced spin-state switching effect (CISSS). By determination of association constants and thermodynamic parameters for the coordination of axial ligands prediction of the switching behaviour of analogous LD-CISSS systems is possible.^[3]

[1] S. Venkataramani, U. Jana, M. Dommaschk, F. D. Sönnichsen, F. Tucek, R. Herges, *Science* **2011**, *331*, 445-448; [2] M. Dommaschk, M. Peters, F. Gutzeit, C. Schütt, C. Näther, F. D. Sönnichsen, S. Tiwari, C. Riedel, S. Boretius, R. Herges, *J. Am. Chem. Soc.* **2015**, *137*, 7552-7555; [3] H. Brandenburg, J. Kraemer, K. Fischer, B. Schwager, B. Flöser, C. Näther and F. Tucek, *Eur. J. Inorg. Chem.* **2018**, 576-585.

Spin State Switching of Transition Metal Complexes with Photoswitchable Ligands in Solution

H.-L. Fitschen*, S. Megow#, F. Temps#, F. Tuczek*

* Prof. Dr. Felix Tuczek, Christian-Albrechts-Universität, Institute of Inorganic Chemistry, Max-Eyth-Str. 2, 24118 Kiel/D

Prof. Dr. Friedrich Temps, Christian-Albrechts-Universität, Institute of Physical Chemistry, Max-Eyth-Str. 1, 24118 Kiel/D

The transition between the low spin and the high spin state in transition metal complexes is called spin crossover (SCO). Most interesting for applications are light-induced spin switching phenomena because they potentially offer temporal and spatial resolution, fast response, and high selectivity. A variety of applications seems possible, for example switchable contrast agents for magnetic resonance imaging (MRI).^[1, 2]

Concerning spin state switching in solution, we focus on two different effects. In the case of the LD-LISC effect (Ligand-Driven Light-Induced Spin Change) an iron(II)-complex with one pentadentate or hexadentate ligand in addition with an azo compound can be isomerized by light which shall influence the ligand field strength, so that the magnetism of the complex may change. In order to better understand the facts of the magnetic change and to examine it on a short time scale, transient UV/Vis measurements were carried out.

Furthermore, we generate transition metal complexes containing iron(II)- or nickel(II)-center which are expected to show the LD-CISS effect (ligand-driven coordination-induced spin state switching). Here, the coordination number is varied by isomerization of a photoswitchable ligand of which only one isomer binds to the metal resulting in a spin change.^[1] The only system which exhibits this effect so far is the so called “record player” based on a nickel-porphyrin.^[1, 3] More recently we focus on non-porphyrin-based, tridentate or tetradentate ligands, for example salicylaldehydes.



Scheme 1: Schematic representation of the LD-LISC and LD-CISS-effect.

References:

[1] S. Venkataramani, U. Jana, M. Dommaschk, F. D. Sönnichsen, F. Tuczek, R. Herges, *Science* 2011, 331, 445–448. [2] M. A. Halcrow, *Spin-Crossover Materials – Properties and Applications*, Wiley-VCH, Weinheim, Germany, 1st ed., 2013. [3] S. Thies, H. Sell, C. Schütt, C. Bornholdt, C. Näther, F. Tuczek, R. Herges, *J. Am. Chem. Soc.* 2011, 133, 16243–16250.

Fragmentation and recombination of Co-based single ion magnets

Ling Fu, Winfried Plass, Richard Berndt, Manuel Gruber

Institut für Experimentelle und Angewandte Physik, Christian-Albrechts-Universität zu Kiel, 24098 Kiel, Germany

Single-ion magnets have promising prospects in molecular spintronics and quantum computing. However, these compounds are relatively fragile, such that their integrity and properties may be strongly affected by

adsorption on surfaces. We sublimed $\text{Co}(\text{NphNO}_2)_2$ single-ion magnets on Au(111) surfaces. Using low-temperature scanning tunneling microscopy, we evidence that these molecules are fragmented on the surface. The $(\text{NphNO}_2)_2$ ligand form interesting assemblies with no trace of Co atoms. Upon further deposition of Co atoms and annealing, we observe two new types of complexes on the surface, which probably result from the bonding of the Co atoms to the ligands. Interestingly, the dI/dV spectra on these complexes exhibit features compatible with a Kondo resonance.

Influence of Surface Adsorption on the Integrity and Functionality of a novel Fe(II) Spin-Crossover Compound

Jan Grunwald¹, S. Rohlfs², M. Gruber², B. M. Flöser¹ and F. Tuczek¹.

¹ Institut für Anorg. Chemie, Christian-Albrechts-Universität zu Kiel, 24098 Kiel, Germany, jgrunwald@ac.uni-kiel.de.

² Institut für Exp. und Angew. Physik, Christian-Albrechts-Universität zu Kiel, 24098 Kiel, Germany.

Bistability between two distinct states of a system is an important feature for several applications, such as sensors, displays or electronic storage devices. This can, for example, be accomplished by transition metal complexes with an electron configuration of $3d^4$ to $3d^7$, which can undergo a Spin Crossover. Depending on the metal center and the ligands, those complexes can be either in a High Spin state ($S=2$ for Fe^{II}) or in a Low Spin state ($S=0$ für Fe^{II}). Also, parameters such as temperature, pressure or light (i. e. *light induced excited spin state switching*, LIESST) can influence the stability of the two states and can thus be used as external stimuli to switch reversibly between them. For the application of these systems, it is necessary to apply them as thin films on substrates. One method to do so is the physical vapor deposition (PVC, i.e. sublimation). Besides classical Spin Crossover complexes such as $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$, this was shown mostly for FeII complexes with varying borate ligands on several surfaces ($[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{phen})]$ etc. on HOPG, Bismuth and others).^[1-3]

With $[\text{Fe}(\text{pyr}(\text{CF}_3)_2)_2(\text{phen})]$, we were recently able to show successful PVC for a new complex that is not based on borate ligands. This complex shows thermal SCO and LIESST as a film (40 ML on TiTe_2 , HfS_2) with a spin transition temperature $T_{1/2}$ of about 330 K, while it is nominally a Low Spin compound in bulk material.^[4]

In a follow-up study, we investigated the same molecule in submonolayers on various semi-conducting substrates as well as on Au(111) and a layer of graphene on Ni(111). While we found the first layer of molecules to be broken on Au(111), part of the molecules were indeed intact and functional on graphene on Ni(111). Through careful analysis of the data, we were able to determine that the molecules are not partially locked in the High Spin state as one might expect, but rather that 30 % of the molecules were broken on this intermediary substrate between metals and semiconductors.^[5]

CHX), the enolic structure is favored (>90%), whereas in polar solvents the diketo form coexists in high concentration (e.g. ~40% diketo in acetonitrile, ACN). However, owing to the weak oscillator strength of the forbidden $1n\pi^*$ transition of the diketo tautomer, selective photoexcitation of the enol form can be assured regardless of the solvent used. Here, we report on the ultrafast electronic relaxation and intramolecular reaction dynamics of the prototypical β -diketone acetylacetone (AcAc) in its enol form upon photoexcitation at $\lambda=266\text{nm}$ to the $S_2(1\pi\pi^*)$ state in CHX and in ACN. The ensuing processes were probed by means of femtosecond transient vibrational absorption spectroscopy (TVAS) which allows for chemical structure-sensitive detection. Following ultrafast (<1 ps) internal conversion from the initially prepared $S_2(1\pi\pi^*)$ to the optically dark $S_1(1n\pi^*)$ state, with partial return of the molecules from $S_1(1n\pi^*)$ to the initial (Z)-enol form in the S_0 state in ~10ps, the formation of a long-lived photoproduct was observed on the nanosecond timescale. Aided by ab initio vibrational frequency calculations, this product could be identified as the previously proposed, but to date elusive (E)-enol form of acetylacetone in the electronic ground state that arises by torsion about the C=C double bond by 180° at the S_1/S_0 conical intersection. Intersystem crossing to the $T_1(3\pi\pi^*)$ state accounts for the third deactivation channel. In contrast to measurements in the gas phase, where photo-induced fragmentation is observed, the reported deactivation and reaction pathways underline the pronounced influence of the solvent.

Light-driven molecular Assemblers for the artificial Phosphate condensation

Daniel Hugenbusch

Otto-Diels-Institut für Organische Chemie, Otto-Hahn-Platz 4, 24118 Kiel

Inspired by the highly sophisticated process of photosynthesis, this work focuses on the development and synthesis of molecular assemblers which are able to selectively condensate monophosphate to diphosphate. The ditopic ligand consists of two binding sites, for example zinc triazacyclononane or zinc dipicolylamine units, each coordinating one monophosphate molecule. These coordination units are connected via a photoswitchable unit. In contrast to the prominent azobenzene, we are using the diazocine as a photoswitch, which is well investigated within our working group and offers highly superior photochemical properties and a much more well-defined movement. The final ditopic assembler has two states, of which one preferentially binds the reactants, while the other binds the product. Being able to reversibly switch between these conformational states offers the possibility to exergonically drive the condensation reaction, which is endergonic in solution, thus forcing the reaction away from thermodynamic equilibrium. As a model system we are using vanadate, which offers certain advantages over phosphate. While the ATP synthase depends on a proton gradient as energy supply, the power source for our assemblers is light, offering the advantage of high spatial and temporal resolution and leaving no trace after being switched off. In analogy to photosynthesis, we will therefore be able to convert light energy into chemical energy and realise an important contribution to the machine-like fabrication of molecules.

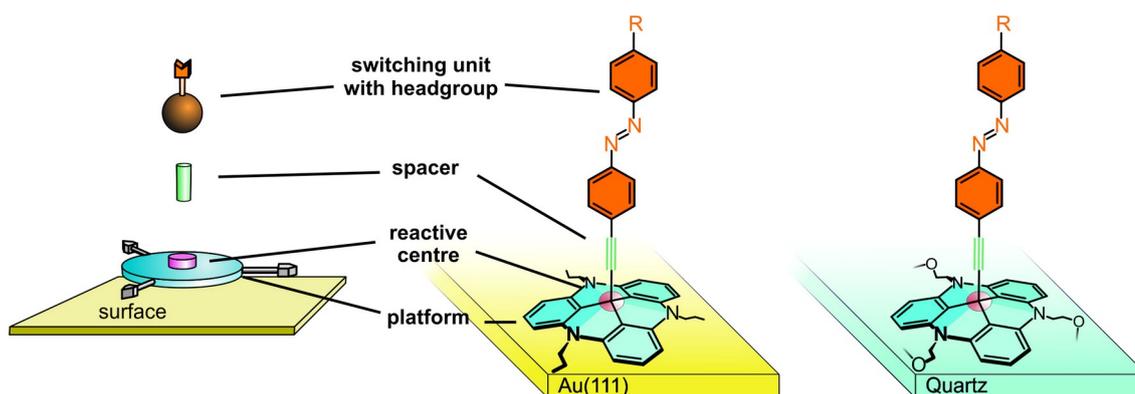
Mounted switches on surfaces

Torben Jäkel¹, Nicolai Krekieh², Olaf M. Magnussen² and Rainer Herges¹

¹Otto Diels Institute for Organic Chemistry, Christian-Albrechts-University, Kiel, 24118 Germany, E-mail: tjaekel@oc.uni-kiel.de

²Institute for Experimental and Applied Physics, Christian-Albrechts-University, Kiel, 24118 Germany

The TATA concept developed by the Herges group is based on triazatriangulenium molecules (TATA) which build highly ordered self-assembled monolayers on gold surfaces. That concept allows us to deposit functional molecules orthogonally on the surface reaching into the free space above. By choosing different sidechains it is possible to define the distance between these molecules. This way we are able to functionalise surfaces with several functional molecules e. g. azobenzenes or porphyrins. Depending on these results we expand this concept to quartz surfaces on which we are able to deposit TATA platforms covalently. With this approach we are now able to functionalize quartz surfaces with azobenzene. Due to the properties of the quartz surface we can analyse the monolayers via UV vis spectroscopy. Furthermore we want to mount porpyhrins on quartz surfaces and detect their fluorescence. With the incorporation of a photoswitchable unit we want to observe fluorescence quenching on the quartz surfaces.



References

- ^[1] B. Baisch, D. Raffa, U. Jung, O.M. Magnussen, C. Nicolas, J. Lacour, J. Kubitschke, R. Herges, *J. Am. Chem. Soc.* **2009**, *131*, 442–443.
- ^[2] J. Kubitschke, C. Näther, R. Herges, *Eur. J. Org. Chem.* **2010**, *26*, 5041–5055.
- ^[3] F. L. Otte, S. Lemke, C. Schütt, N. R. Krekieh, U. Jung, O. M. Magnussen, R. Herges, *J. Am. Chem. Soc.* **2014**, *136*, 11248–11251.

Electron spin resonance by radio-frequency scanning tunneling microscopy

N. Kalantari, T. Jürgens, R. Woltmann, A. Weismann, R. Berndt and M. Gruber

Institut für Experimentelle und Angewandte Physik, Christian-Albrechts-Universität zu Kiel, 24098 Kiel, Germany

Electron spin resonance scanning tunneling microscopy (ESR-STM) is a new developing surface science technique, which allows to combine high spatial resolution with high energy resolution (several neV in contrast to meV for conventional STM) [1]. The working principle relies on the application of radio-frequency voltages (several GHz) to the STM junction. In certain conditions, a spin resonance can be driven, which is detected as a change in the spin-polarized tunneling current. The main instrumental difficulty is to

transmit radio frequencies of constant amplitude over a wide frequency range (DC-40GHz) [2,3,4]. Furthermore, the instrument should be equipped with a magnet to tune the energy of the spin resonance.

Here, we describe the upgrading of a low-temperature STM by adding high-frequency cables (DC-40GHz) and a superconducting magnet ($B_z = 1$ T). The transmission line consists of several cables to ensure (i) high radio-frequency transmission, (ii) adequate thermal properties and (iii) mechanical flexibility. We show that the selection of cables is critical for the transmission. This setup will soon be employed to investigate the spin within molecular complexes and to explore the magnetic interactions between molecules.

References

- [1] Baumann, S., Paul, W., Choi, T., Lutz, C. P., Ardavan, A., & Heinrich, A. J. (2015). Electron paramagnetic resonance of individual atoms on a surface. *Science*, 350 (6259), 417-420.
- [2] Hervé, M., Peter, M., & Wulfhekel, W. (2015). High frequency transmission to a junction of a scanning tunneling microscope. *Applied Physics Letters*, 107 (9), 093101.
- [3] Paul, W., Baumann, S., Lutz, C. P., & Heinrich, A. J. (2016). Generation of constant-amplitude radio-frequency sweeps at a tunnel junction for spin resonance STM. *Review of Scientific Instruments*, 87(7), 074703.
- [4] Natterer, F. D., Patthey, F., Bilgeri, T., Forrester, P. R., Weiss, N., & Brune, H. (2019). Upgrade of a low-temperature scanning tunneling microscope for electron-spin resonance. *Review of Scientific Instruments*, 90(1), 013706.

NFDI4Chem: Shaping a Digital and Cultural Change for Research Data Management in Chemistry

Oliver Koepler

Technische Informationsbibliothek on behalf of the NFDI4Chem consortium

The question of how we organise the increasing amount of research data is more pressing than ever. The increasing importance and value of mostly born-digital research data is also reflected in the "Guidelines for Safeguarding Good Scientific Practice" Code of the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) which has come into force on 1 August 2019. How do we address these requirements? How can data be stored in the long term and made accessible beyond the research group or institution itself? In what data formats and where can research data be stored? With the FAIR Data Principles, a framework has been formulated for making data "findable, accessible, interoperable, and reusable" in the scientific process.^[1]

In this context, Germany is preparing to develop a national infrastructure for research data. As part of this, NFDI4Chem is an effort by the German chemistry community to develop and maintain a national research data infrastructure for the research domain of chemistry in Germany. The vision of NFDI4Chem is the application of digitisation principles to all key steps of research in chemistry. NFDI4Chem supports scientists in their efforts to collect, store, process, analyse, disclose and re-use research data. Measures to promote Open Science and Research Data Management (RDM) in agreement with the FAIR data principles are fundamental aspects of NFDI4Chem to serve the community with a holistic concept for access to research data. NFDI4Chem aims to represent all disciplines of chemistry in academia and industry. In the initial phase, NFDI4Chem focuses on handling data of molecules and data of their characterisation and reactions, both experimental and theoretical.

In this poster, we will outline the concepts of NFDI4Chem to support research data management throughout the research process and make open science in chemistry a reality.

[1] M.D. Wilkinson, M. Dumontier, I.J.J. Aalbersberg, G. Appleton, M. Axton, A. Baak, N. Blomberg, J.-W. Boiten, L. B. da Silva Santos, P. E. Bourne et al., *Scientific data* **2016**, 3, 160018.

Synthesis And Characterization Of Photoswitchable Receptors For Oxoanion Condensation

Fabian Kruse, Prof. Dr. Rainer Herges

Otto-Diels-Institut für Organische Chemie, Otto-Hahn-Platz 4, 24118 Kiel, fkruse@oc.uni-kiel.de

In nature complex biomolecules are synthesized by molecular machines powered by ATP.^[1,2] Following the principles of nature light-driven molecular assemblers were designed. They drive systems away from thermodynamic equilibrium to build up more complex structures. Thereby light is converted to chemical energy. In a mixture of compounds the desired reactants are selected and guided along the preferred reaction channel to form complex molecules which could not be obtained in a spontaneous process. This concept should be realized with receptors containing two zinc-cyclene units as binding sites for oxoanions^[3] and a photo-switchable azobenzene unit.^[4] The desired endergonic condensation to high-energy oligomers is then achieved by light-induced configuration change (*cis-trans*-isomerisation). Based on quantum mechanical calculations a tennis ball-shaped structure for the complexation of tetravanadate by two receptor molecules has been postulated. A novel approach is the covalent linkage of two monomers to a macrocycle (fig.1), which allows a preferred formation of the “tennis ball” complex due to the pre-orientation and entropic favorable balance of number of particles. This should suppress the formation of polymers and verify the assumed structure, resulting in important findings on the way of developing a light-driven molecular assembler.

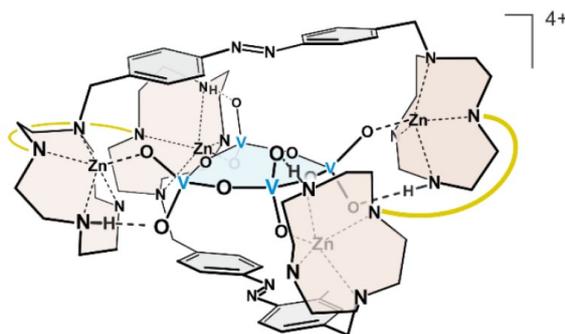


Figure 1: Covalent linkage of two receptor molecules for the complexation of tetravanadate.

References

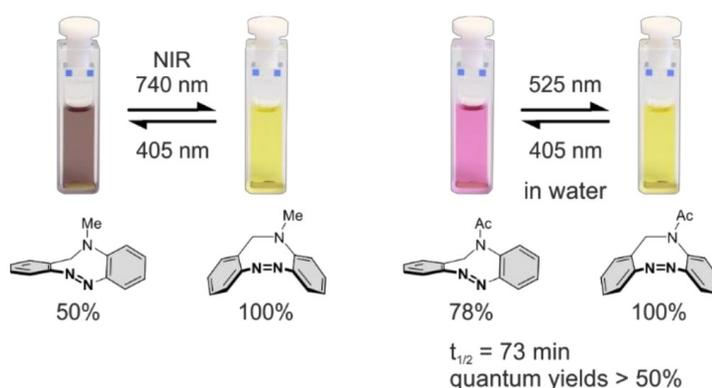
1. J. E. Walker, *Angew. Chem. Int. Ed.* **1998**, 37, 2308-2319.
2. P. D. Boyer, *Angew. Chem. Int. Ed.* **1998**, 37, 2296-2307.
3. H. Sell, A. Gehl, F. D. Sönnichsen, R. Herges, *Beilstein J. Org. Chem.* **2012**, 8, 81-89.
4. H. Sell, A. Gehl, D. Plaul, F. D. Sönnichsen, C. Schütt, F. Köhler, K. Steinborn, R. Herges, *Commun. Chem.* **2019**, 2, 1-6.

Nitrogen Bridged Diazocines: Photochromes Switching within the Near-Infrared Region with High Quantum Yields in Organic Solvents and in Water

Pascal Lentjes, Rainer Herges

Otto Diels Institute of Organic Chemistry, Christian-Albrechts-University, 24118 Kiel, Germany, plentes@oc.uni-kiel.de

Diazocines are bridged azobenzenes with superior photophysical properties. In contrast to azobenzenes the *Z* configuration is thermodynamically stable and the *E* isomer is metastable. We present a new class of nitrogen bridged diazocines with bathochromically shifted switching wavelengths and remarkably high quantum yields (-NH-CH₂-bridged diazocine: $\Phi_{Z \rightarrow E} = 0.57$, $\Phi_{E \rightarrow Z} = 0.8$). *Z* to *E* isomerization is induced by irradiation with blue light, whereas switching back to the *Z* isomer is accomplished with light in the near-infrared window (up to 740 nm), which is important for medical applications like photopharmacology (deep tissue penetration). Furthermore, substitution at the bridging nitrogen should provide access to widely applicable tricyclic, photoswitchable pharmacophores. The -NAc-CH₂- bridged derivative is soluble in water and all photophysical properties (conversion rates, quantum yields and thermal half-lives) are largely retained. Hence, this diazocine is an ideal photoswitch for applications in biochemical systems and in photopharmacology.



Thiophene-based S,N-Heteroacenes: Electronic Properties and X-Ray Structure Analysis

Elena Mena-Osteritz

In this contribution, the photophysical behavior of series of linear S,N- and Se,N-heteroacenes showing a planar pi-delocalized system will be discussed. With the help of theoretical calculations the electronic properties of those systems will be correlated with experimental findings.

Fe(II) SCO Complexes: Influence of Cooperativity in Bulk and Film

Sascha Ossinger^a, Holger Naggert^a, Lalminthang Kipgen^b, Eckhard Billc, Matthias Bernien^b, Wolfgang Kuch^b and Felix Tuczek^a

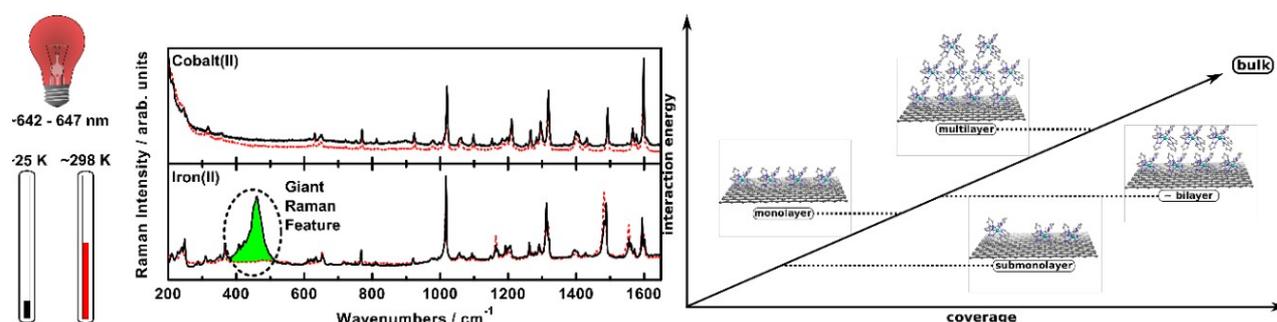
a: Christian-Albrechts-Universität zu Kiel, Institut für Anorganische Chemie, Max-Eyth-Straße 2, 24118 Kiel, Germany

b: Freie Universität Berlin, Institut für Experimentalphysik, Arnimallee 14, 14195 Berlin, Germany

c: Max Planck Institute for Chemical Energy Conversion, Stiftstrasse 34-36,

45470 Mülheim an der Ruhr, Germany

email: sossinger@ac.uni-kiel.de



Spin crossover transition-metal complexes ($3d^4 - 3d^7$) continue to be a fascinating class of functional materials in the field of coordination chemistry and have the potential to play a significant role in electronic data storage as spintronics. Transitions between the diamagnetic low spin (LS, $S=0$ for FeII) and the paramagnetic high-spin (HS, $S=2$ for FeII) state of these complexes can be induced by stimuli like temperature and light (LIESST/reverse-LIESST). For applications it is necessary to get them as thin films on substrates. The physical vapour deposition proved to be the optimal method. Amongst other we have shown this for various complexes with organoborate ligands on different substrates.^[1-4]

We have shown for $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{bipy})_2]$ the evolution of cooperativity in the spin transition on a highly oriented pyrolytic graphite surface, using x-ray absorption spectroscopy.^[5] On increasing the coverage from ~ 0.35 to ~ 10 monolayers, the width of the temperature-induced spin transition curve narrows significantly, evidencing the buildup of cooperative effects.

More recently, we have shown for a few complexes of the type $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{L})_2]$ (L = diamine ligands) the influence of cooperativity effects in form of π - π -stacked dimers on the so-called observed giant Raman feature.^[6]

[1] H. Naggert et al., Dalton Trans. 2011, 40, 6364-6366.

[2] T.G. Gopakumar et al., Angew. Chemie Int. Ed. 2012, 51 (25), 6262-6266.

[3] M. Bernien et al., ACS Nano 2015, 9, 8960-8966.

[4] S. Ossinger et al., J. Phys. Chem. C. 2017, 121 (2), 1210-1219.

[4] L. Kipgen, M. Bernien, S. Ossinger et al., Nat. Commun. 2018, 9, 2984.

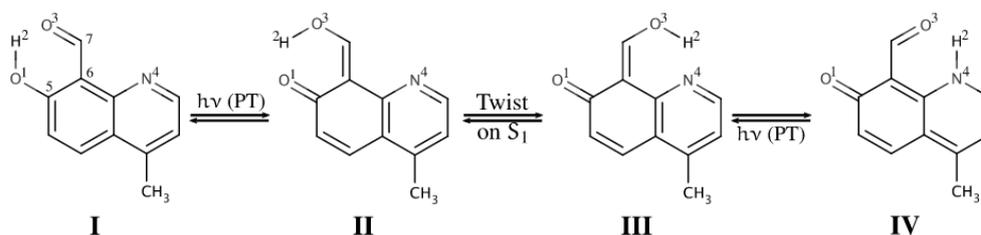
[5] S. Ossinger et al., Inorg. Chem. 2019, submitted.

Full-Dimensional Photodynamics of Bistable Proton Transfer Switches

Tim Raeker, Bernd Hartke^a

Institut für Physikalische Chemie, Christian-Albrechts-Universität zu Kiel, Olshausenstraße 40, Kiel (Germany)

Excited-state intramolecular proton transfer (ESIPT) reactions are one of the fastest in chemistry (<100 fs) which – among other features like high photostability – makes them a viable reaction class for molecular switches. ESIPTs can be coupled with double bond rotation/isomerization, so that molecules can act as “molecular cranes”, facilitating long-range proton transfer. A versatile model system is 7-hydroxy-4-methylquinoline-8-carbaldehyde (HMQCA): it features two proton-accepting sites, two stable ground-state isomers and should allow for easy derivatization. There is also experimental and theoretical reference data available, however, only for static properties, e.g., ground-state IR spectra or potential energy surface scans.



In this contribution we show the results of the full-dimensional surface-hopping molecular dynamics (MD) of HMQCA and two derivatives after photo-excitation. The MD calculations were performed with semiempirical quantum chemistry coupled to floating-occupation configuration interaction. This setup was also benchmarked against ab initio and density functional theory methods. Furthermore, we present a concept for system-specific parameter optimization for the semiempirical model.

Long-Distance Rate Acceleration by Bulk Gold

Alexander Schlimm

Institut für Anorganische Chemie, Otto-Hahn-Platz 6, 24118 Kiel

We report on a very unusual case of surface catalysis involving azobenzenes in contact with a Au(111) surface. We observe a rate acceleration (up to 1300-fold) of cis-trans isomerization on gold, compared to solution. By using carefully designed molecular frameworks we are able to systematically tune the electronic coupling to the surface. The isomerization kinetics of molecules with very weak coupling to the metal is similar to that found in solution. For their counterparts with strong coupling the relaxation rate is shown to depend on the spin density distribution in the triplet states of the molecules. This suggests that an intersystem crossing is involved in the relaxation process. Besides their impact on catalytic processes, these effects could be used to trigger reactions over long distances.

Light-controlled Rabi Splitting in an Ultra-strongly Coupled Surface Plasmon Polariton-Exciton System

Bill Brook Shurtleff, Faculty of Engineering, Kaiserstraße 2, 24143 Kiel

The all-optical control of physical properties could be of interest for many applications, e.g. complete information processing by light. Here we show that the degree of Rabi splitting can be optically controlled in a system where surface plasmon polaritons excited at a metal-polystyrene interface on a prism in a Kretschmann configuration couple to excitons of the merocyanine conformation of spirooxazine dye dispersed in the polystyrene matrix resulting in the formation of hybrid modes (see Fig. 1). The degree of the splitting depends on the concentration of dye molecules and on the exposure to UV-light. Measurements were done using spectroscopic ellipsometry which not only permits in situ observation of Rabi splitting during UV exposure but also, once switched, rapid measurement of the dispersion relation with an avoided crossing of the resultant non-radiative modes. Rabi splitting of ~ 600 meV and $\sim 29\%$ of the molecular transition energy attests to the ultra strong coupling regime.

Investigating the Perceptions of Students on Nature of Scientists Aspects and Authenticity in Learning Environments

Insa Stamer, IPN - Leibniz Institute for Science and Mathematics Education at Kiel University, Olshausenstraße 62, D-24118 Kiel

Primary objective of the thesis is the development of authentic learning situations in out-of-school student laboratories. High school students have diverse suggestions and ideas of a researcher's work. The university laboratory klick! in Kiel allows visiting students to conduct and observe research-based experiments in nano science. Providing videos of people working on relevant and up to date scientific topics, students may get a more realistic impression of the work in science. The different perceptions and prejudices that students have of the everyday work in a research environment have been described as Nature of Scientists (NoSt) aspects (Wentorf, 2016). To measure the effect of video presentations shown prior to the experimental part, pre- and post-test questionnaires were used. The results show increasing effects in previously underestimated work fields of scientists.