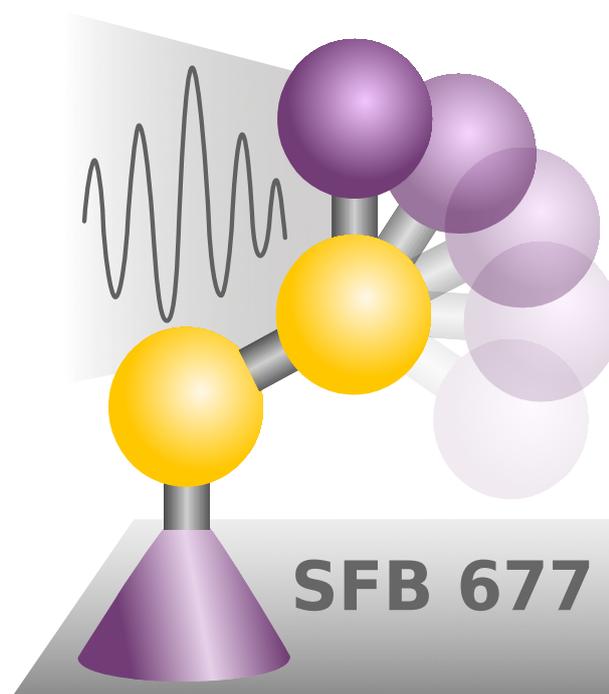


Third SFB Conference

Molecular Switches: Elementary Processes and Applications

August 27 - 30, 2017

Fielmann Akademie, Schloss Plön



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 2017]

VENUE

The third 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

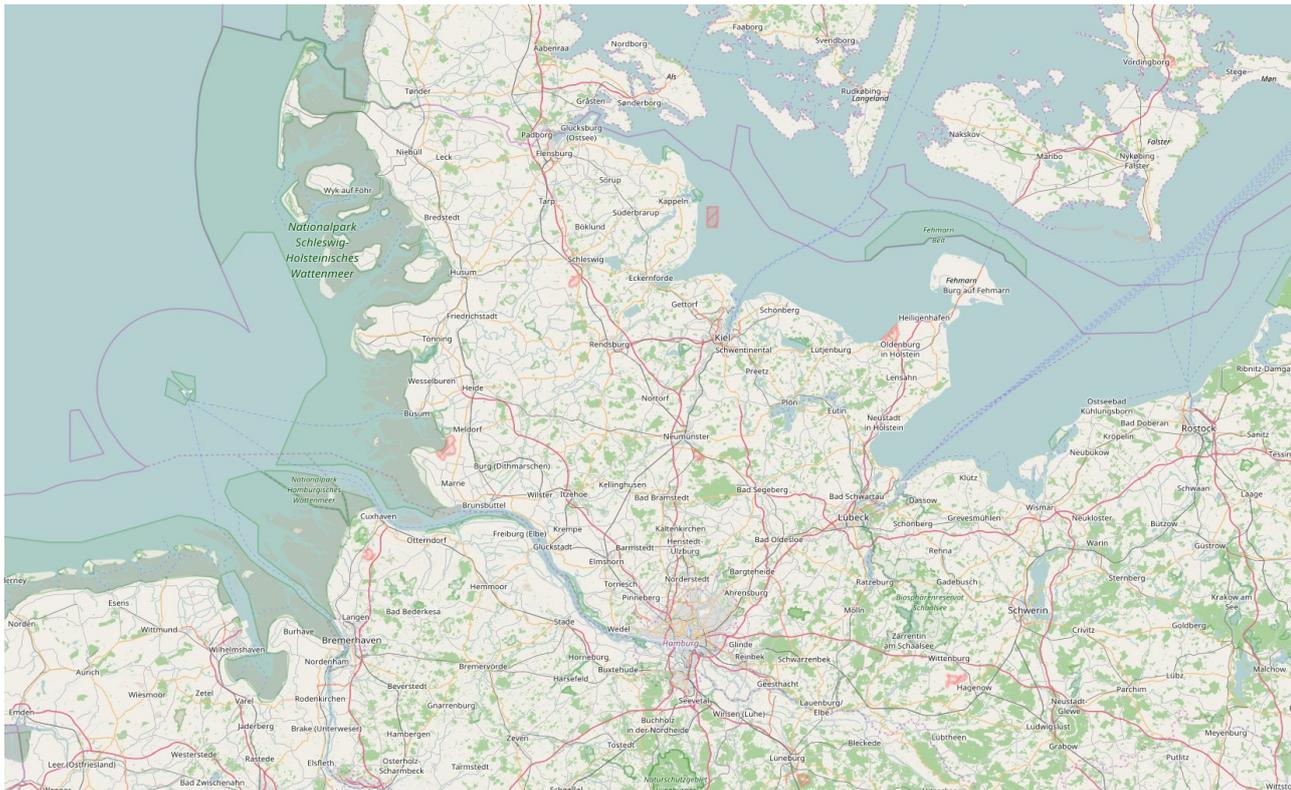


lecture hall



boat excursion

LOCATION



SHORT SCHEDULE

Sunday, 27. Aug. 2017		Monday, 28. Aug. 2017				Tuesday, 29. Aug. 2017				Wednesday, 30. Aug. 2017			
	07:00	breakfast		breakfast		breakfast		breakfast		breakfast		breakfast	
	09:00	Leonard	Strasbourg	chair		Ernst	Dübendorf	chair		Klajn	Rehovot	chair	
	09:30	B09	Kiel			Lienau	Oldenburg			B12	Kiel		
	09:50	A03	Kiel			C12	Kiel			A06	Kiel		
	10:10	Repain	Paris			A01	Kiel			C13	Kiel		
	10:40	coffee break 11:00 – 11:30				coffee break 11:00 – 11:30				coffee break 10:30 – 11:00			
	11:30	A07	Kiel	chair		Katsonis	Twente	chair		B06/B07	Kiel	chair	
	11:50	B11	Kiel			Schöll	Würzburg			B10	Kiel		
	12:10	Wöll	Karlsruhe			A08	Kiel			McConnell	Kiel		
	12:50	lunch 13:00 – 14:00				lunch 13:00 – 14:00				lunch 13:00 – 14:00			
	14:00 – 16:00	poster session				chair				closing remarks			
	16:00	registration		chair		Prosenc	Kaisersl.	chair		lunch		Herges	
	16:00	Leigh	Manchester			C14	Kiel			departure			
	16:30	C01	Kiel			Bräse	Karlsruhe			departure			
	16:50	B13	Kiel			15:30 departure				12:45 lunch			
	17:10	Wegner	Gießen			16:00 – 18:00 boat-trip				14:00 departure			
	19:30	dinner	dinner			conference dinner							

DETAILED SCHEDULE

Sunday, 27.08.2017

13:00 ***arrival***

16:00 ***registration***

18:00 ***welcome reception***

award ceremony: KINSIS award 2017

award lecture: ***Marcel Dommaschk, Manchester, UK***

Photoswitchable contrast agents for MRI

19:30 ***dinner***

Monday, 28.08.2017

07:00 ***breakfast***

09:00 ***Jérémie Léonard, Strasbourg, France***

Vibrationally coherent optomechanical energy transduction in biomimetic molecular switches.

09:30 ***SFB 677 project B9, Roland Löw, Talina Rusch, Alexander Schlimm, Kiel***

Functionalization and Investigation of Azo Functionalized TATA Platforms

09:50 ***SFB 677 project A3, Florian Gutzeit, Kiel***

Spin Switching of Transition Metal Complexes

10:10 ***Vincent Repain, Paris, France***

Voltage and light induced spin switch of spin-crossover molecular monolayer on surfaces

10:40 ***coffee break***

11:30 ***SFB 677 project A7, Hendrik Boehnke, Kiel***

Photo-Induced Dynamics of H-Transfer Switches

11:50 ***SFB 677 project B11, Vivek Poonthiyil, Kiel***

Photoswitching of Bacterial Adhesion

- 12:10 ***Christof Wöll, Karlsruhe, Germany***
Liquid Phase Epitaxy of Molecular Frameworks on Solid Substrates: A New Class of Designer Solids?
- 12:40 ***lunch***
- 14:00 ***poster session***
- 16:00 ***David Leigh, Manchester, UK***
Making the Tiniest Machines
- 16:30 ***SFB 677 project C1, Franz Faupel, Kiel***
Light-Induced Conductance Switching in Photomechanically Active Carbon Nanotube-Polymer Composites
- 16:50 ***SFB 677 project B13, Sebastian Rohlf, Kiel***
NEXAFS study of novel robust spin crossover films on metallic surfaces
- 17:10 ***Herrmann Wegner, Gießen, Germany***
Azobenzene switches – from physical organic chemistry to energy storage
- 19:30 ***dinner***

Tuesday, 29.08.2017

- 07:00 ***breakfast***
- 09:00 ***Karl-Heinz Ernst, Dübendorf, Switzerland***
Helical molecules at surfaces: selective chemistry and molecular machines
- 09:30 ***Christoph Lienau, Oldenburg, Germany***
Ultrafast multidimensional spectroscopy of charge-transfer processes in light-harvesting systems
- 10:00 ***SFB 677 project C12, Christian Peifer, Kiel***
A Photoswitchable Kinase Inhibitor: Photoinduced E/Z Isomerization of Axitinib
- 10:20 ***SFB 677 project A1, Friedrich Temps, Kiel***
Ultrafast Photo-induced Dynamics of the Magnetically Bistable Azopyridine/Ni-Porphyrin Record Player Spin Switch

- 10:40 ***coffee break***
- 11:30 ***Nathalie Katsonis, Twente, The Netherlands***
title not yet available at press date – please see website
- 12:00 ***Achim Schöll, Würzburg, Germany***
Orbital Imaging by Angle Resolved Photoelectron Spectroscopy: From Basic Principles to High Resolution Experiments and Limitations
- 12:30 ***SFB 677 project A8, Lisa Leben, Fabian Kruse, Kiel***
Function by Switching: Molecular Assemblers, Molecular Machines Performing Synthesis
- 12:50 ***lunch***
- 14:00 ***Marc Heinrich Prosenc, Kaiserslautern, Germany***
Covalently Linked Magnetic Complexes on Surfaces: Spin Delivery, Logic Devices and Photo-Switches
- 14:30 ***SFB 677 project C14, Sindu Shree, Kiel***
Polymer Composite Inspired by the Human Skin: Molecular Switches in Complex Environments - Progress Report on Mechanophoric Composites
- 14:50 ***Stefan Bräse, Karlsruhe, Germany***
Design and synthesis of novel molecular switches - from small molecules to materials
- 15:30 ***departure for excursion***
- 16:00 ***boat excursion***
- 19:30 ***conference dinner***

Wednesday, Aug 30

- 07:00 ***breakfast***
- 09:00 ***Rafal Klajn, Rehovot, Israel***
Reversible photochromism in the cavities of flexible coordination cages

- 09:30 **SFB 677 project B12, Malte Großmann, Kiel**
Light-Triggered Control of Plasmonic Refraction and Group Delay by Photochromic Molecular Switches
- 09:50 **SFB 677 project A6, Rainer Herges, Jens Gröbner, Kiel**
Magnetic Resonance Imaging Setups for Photo-Switchable Contrast Agents
- 10:10 **SFB 677 project C13, Bridget Murphy, Kiel**
Structure and Kinetics of Switching in Phospholipid Membranes
- 10:30 **coffee break**
- 11:00 **SFB 677 projects B6, B7, Manuel Gruber, Kiel**
Switching of single molecules on metallic surfaces
- 11:20 **SFB 677 project B10, Stefan Heinze, Kiel**
Anisotropic magnetoresistance at the single molecule level
- 11:40 **Anna McConnell, Kiel**
Transformation of an Iron(II) Cage from High- to Low-Spin Switches Guest Release in a Two Cage System
- 12:00 **Giovanni Granucci, Pisa, Italy**
Simulating the photoisomerization of self assembled monolayers of azobiphenyls
- 12:30 **closing remarks**
- 12:45 **lunch**
- 14:00 **departure**

ABSTRACTS FOR LECTURES

in alphabetical order of speakers

Photo-Induced Dynamics of H-Transfer Switches

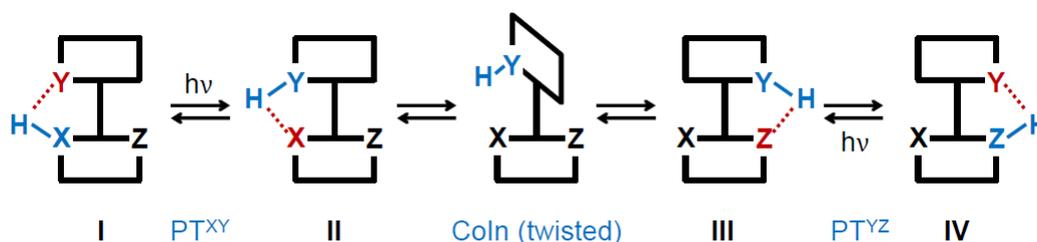
Hendrik Böhnke¹, Sebastian Megow¹, Rebecca Stellmacher¹, Tim Raeker¹,

Jesper Rönn², Ulrich Lüning², Bernd Hartke¹ and Friedrich Temps¹

¹ *Institute of Physical Chemistry, Christian-Albrechts-University Kiel*

² *Institute of Organic Chemistry, Christian-Albrechts-University Kiel*

Bistable intramolecular H-transfer systems exhibit a huge potential as photochromic molecular switches as they often feature electronic deactivation on an ultrafast timescale. Thus, undesired side reactions are virtually eliminated, thereby enabling record numbers of switching cycles. Within the scope of the Kiel CRC, special interest is drawn to such bistable intramolecular H-transfer switches in a joint effort of organic synthesis, theoretical calculations and spectroscopic experiments. Amongst others, we focus on a new design for photoreversible H-transfer switches, which has recently been proposed on the basis of theoretical quantum chemical calculations [A. L. Sobolewski, *Phys. Chem. Chem. Phys.* **2008**, 10, 1243].



According to this scheme, photoexcitation initiates an ultrafast H-transfer in the excited state from a donor site to an intermediate acceptor group. Following a large-amplitude torsional motion driven by electronic deactivation through a conical intersection with the electronic ground state, the proton is finally dropped at its acceptor site. As a net result, the proton is transported along the molecular scaffold. Here, we report on recent results of femtosecond time-resolved spectroscopy, quantum chemical calculations and organic synthesis towards such bistable photochromic switches. Emphasis is put on the direct observation of the H-transfer pathway of N-(3-pyridinyl)-2-pyridine-carboxamide (NPPCA) on the sub-picosecond timescale by combined time-resolved fluorescence, electronic and vibrational absorption spectroscopy aided by theoretical calculations. In addition, first experimental and theoretical results will be reported for novel other H-transfer switches, including newly synthesized hydroxyquinoline-based ones.

Design and synthesis of novel molecular switches - from small molecules to materials

Stefan Bräse
KIT, Karlsruhe, Germany

In this talk, various new materials using supramolecular and/or covalent linking from various symmetrical organic building blocks are presented. Photoswitching using azobenzenes and other photoswitches will be discussed in Terms of design, Synthesis, efficiency and applications.

Helical molecules at surfaces: selective chemistry and molecular machines

Karl-Heinz Ernst^{1,2}

¹Nanoscale Materials Science, Empa, Swiss Federal Laboratories for Materials Science and Technology, Überlandstrasse 129, CH-8600 Dübendorf, Switzerland

²Department of Chemistry, University of Zurich, Winterthurerstr. 190, CH-8057 Zürich, Switzerland

Molecular recognition among chiral molecules on surfaces is of paramount importance in biomineralization, enantioselective heterogeneous catalysis, and for the separation of chiral molecules into their two mirror-image isomers (enantiomers) via crystallization or chromatography. Understanding the principles of molecular recognition in general, however, is a difficult task and calls for investigation of appropriate model systems. One popular approach is thereby studying intermolecular interactions on well-defined solid surfaces, which allows in particular the use of scanning tunneling microscopy (STM). Examples of chiral amplification via the so-called 'sergeant-and-soldiers' effect as well as manipulation of chiral adsorbates via inelastic electron tunneling will be presented. Moreover, we report spin-dependent filtering of electrons by monolayers of these helical molecules. Finally the first successful electrical current-driven, unidirectional motion of a synthetic molecule on a surface will be presented.

Light-Induced Conductance Switching in Photomechanically Active Carbon Nanotube-Polymer Composites

V. Schneider,¹ O. Polonskyi,¹ T. Strunskus,¹ M. Elbahri,² F. Faupel^{1*}

¹Chair for Multicomponent Materials, Faculty of Engineering, Kiel University, Kaiserstr. 2, 24143 Kiel, Germany

²Nanochemistry and Nanoengineering, Department of Chemistry & Materials Science, Aalto University, Kemistintie 1, C321, 00076 Aalto, Finland

*ff@tf.uni-kiel.de

Abstract

Novel optically responsive devices with hosts of potential applications have been demonstrated by coupling carbon nanomaterials with photochromic molecules. For light-induced conductance switching, in particular, azobenzene containing carbon nanotube-polymer nanocomposites proved to be very attractive, providing stable and no-degradable changes in conductivity over time at standard laboratory conditions. In these composites, the photoswitching mechanisms are based on light-induced changes in electronic properties and related to the Pool-Frenkel conduction mechanism. However, no link between conductivity switching and the molecular motion of azobenzene chromophores could be found, due to application of high elastic modulus polymer matrices. Here we report on single wall carbon nanotube-polymer nanocomposites with a soft polycaprolactone polymer host. This system clearly shows the transfer of light induced nano-sized molecular motion to macroscopic thickness changes of the composite matrix. We demonstrate that these photomechanic effects can indeed dominate the conductivity switching behavior over the electronic effects and lead to a reversion of the switching direction near the percolation threshold.

Simulating the photoisomerization of self assembled monolayers of azobiphenyls

Giovanni Granucci

Department of Chemistry and Industrial Chemistry, University of Pisa

We performed a computational investigation of the photodynamics of self assembled monolayers (SAM) of biphenyl azocompounds bound through a terminal S atom to a Gold surface. The *trans* and *cis* SAMs can be interconverted by irradiating with appropriate wavelengths and exhibit quite different structural, optical and electric properties [1, 2, 3]. The photoisomerization shows a cooperative behavior: in a partly isomerized SAM large domains of pure *cis* or *trans* isomers are found [1]. The nonadiabatic dynamics was simulated by the surface hopping method with quantum decoherence corrections. The electronic energies and wavefunctions were computed on the fly with the semiempirical FOMO-CI method in its QM/MM version [4].

Our results show that *cis* \rightarrow *trans* photoisomerization occurs in all the environments. Conversely, *trans* \rightarrow *cis* photoisomerization is suppressed in a pure *trans* SAM, while it occurs in single *trans* molecules embedded in a *cis* SAM. These effect of close packing can explain the previously observed cooperative behavior [1]. Other simulations highlights the role of defects in starting the *trans* \rightarrow *cis* conversion: for example, in a *trans* SAM with a single *cis* molecule, the first neighbors of the *cis* molecule are photoreactive[5]. Moreover, concerning the suppression of photoisomerization, the steric confinement effect appears to be more important than exciton transfer [6].

[1] G. Pace *et al*, PNAS **104**, 9937 (2007).

[2] K. Smaali *et al*, ACS Nano **4**, 2411 (2010).

[3] N. Crivillers *et al*, Adv. Mater. **23**, 1447 (2011).

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[5] V. Cantatore *et al*, J. Phys. Chem. Lett. **7**, 4027 (2016).

[6] E. Titov *et al*, J. Phys. Chem. Lett. **7**, 3591 (2016).

Absolute Temperature Magnetic Resonance Imaging using Photo-Switchable Contrast Agents.

Dr. Jens Groebner, Vanessa Thoms, Dr. Gernot Heitmann, Dr. Marcel Dommaschk, Prof. Rainer Herges
Otto Diels-Institute of Organic Chemistry, CAU Kiel, Otto-Hahn-Platz 4, 24098 Kiel, Germany

Temperature Magnetic Resonance Imaging (MRI) is used for various applications, e.g. tissue ablation using high intensity focussed ultrasound [1] or radio frequency applicators for hyperthermia [2]. For these applications the proton resonant frequency shift (PRF) method [3] is used. Besides PRF techniques based on T_1 -relaxivity [4] or diffusion [5] exist. All MR *intrinsic* methods require reference images and can only be used for relative measurements. Temperature is a clinical marker for increased tissue metabolism and can be used to detect tumours or tissue inflammation [6]. Some temperature MRI contrast agents (CA) exist but they lack of image resolution [7] or use time-consuming MRI spectroscopy [8]. To increase image resolution and shorten measurement time a photo-switchable *record player* CA prototype was developed.

The CA is based on a Ni(II)-porphyrin which is linked covalently with a photo-switchable azoimidazole at one of the *meso* positions. The axial azoimidazole is the tone arm of the so called *record player* molecule and binds in its *cis* form to the Ni(II)-ion. The CA can be switched on (to *cis* form) by light with a wavelength of 365 nm. In the *cis* configuration the complex is paramagnetic (high-spin, $S = 1$) and influences the relaxation times of its solvent (here: MeOH). The isomerisation process back to the *trans* configuration is only temperature dependant.

Calibration measurements with the photo-switchable CA at different temperatures (-7°C to 7°C) were performed in a small animal MR system (ClinScan 7T, Bruker, Ettlingen, Germany) using a cooling jacket with different inversion recovery sequences. For reference a fiber-optical temperature probe (OpSENS, Ville de Québec, Canada) was placed inside the cooling jacket. During imaging the inversion time was set to the off-state of the solution suppressing signal of the solvent. Different CA concentrations were used to determine possible concentration dependencies. To create a temperature gradient and to measure absolute temperature with during standard imaging a custom-built cooling jacket was used. For this purpose the CA and a gel forming agent was dissolved in MeOH to suppress convective flow of heat. A temperature gradient of -5°C to 5°C was used. For imaging a 2D-IR-HASTE sequence with following imaging parameters was used: TR = 10 s, TE = 56 ms, TI = 2.3 s, FoV = $32 \times 32 \text{ mm}^2$, Mtx = $256 \times 256 \text{ px}$, Res = $125 \times 125 \mu\text{m}^2$, SL = 1.1 mm, Repetitions: 360. To increase SNR a temperature map with $144 \times 144 \text{ px}$ was calculated ($222 \times 222 \mu\text{m}$).

Figure 1 shows the mono exponential signal decay at different temperatures (a) and different concentrations (b). The switching of the CA back to its ground state is only temperature dependent.

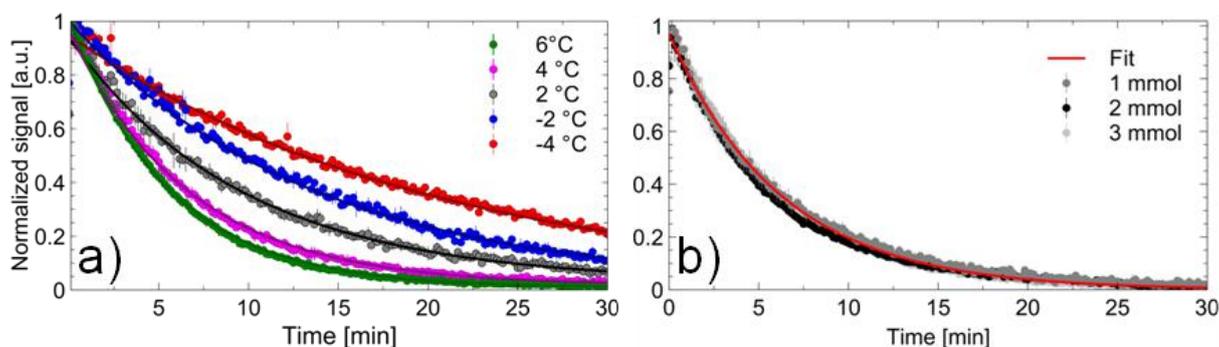


Figure 1: a) MR signal decay at different temperatures. b) MR signal decay at different concentrations.

Figure 2 shows the temperature map of rate constants of the pixel-wise fitted mono-exponential functions. The absolute temperature image clearly shows the gradient from both cold (-5°C) and warm (5°C) compartments of the phantom. With this developed CA it would be possible to perform temperature MRI with standard MR IR sequences during a standard clinical protocol.

For future developments water solubility and increasing the temperature range are planned to perform *in vivo* experiments.

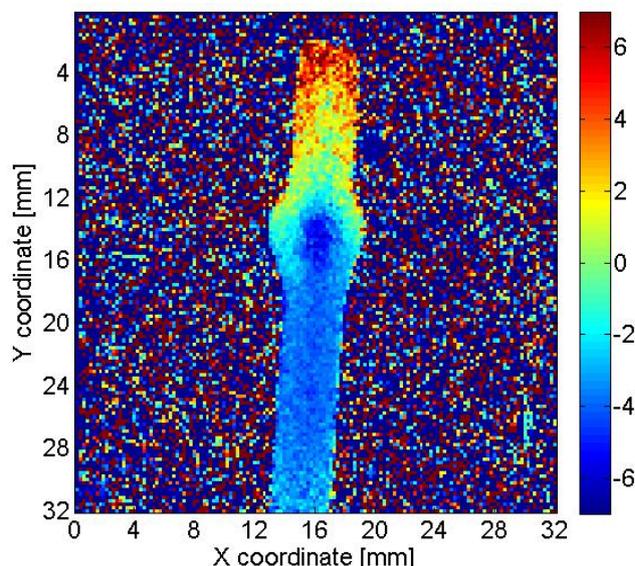


Figure 2: Temperature map calculated from 360 IR HASTE images. Due to low SNR (<10) the resolution of the temperature map was decreased by a factor of 1.8.

[1] Krafft AJ et al. *Med Phys* **2010**, 1: 2380-2393; [2] Dadakova T et al. *Magn Reson Mater Phy* **2015**, 28(4): 305-314; [3] Ishihara Y *Magn Reson Med* **1995**, 34(6): 814-823; [4] Parker DL et al. *Med Phys* **1983**, 10:321-325; [5] Le Bihan D et al. *Radiology* **1989**, 171: 853-857; [6] Jayasundar R et al. *Neuro. India* **2002**, 50:436-437; [7] Heyn CC et al. *NMR Biomed* **2017**, DOI: 10.1002/nbm. 3772; [8] Coman D et al. *NMR Biomed* **2008**, 22:229-239.

Light-Triggered Control of Plasmonic Refraction and Group Delay by Photochromic Molecular Switches

M. Großmann,¹ A. Klick,¹ C. Lemke,¹ J. Falke,¹ M. Black,¹ J. Fiutowski,² A. J. Goszczak,² E. Sobolewska,² A. Usman Zillohu,³ M. Keshavarz Hedayati,⁴ H.-G. Rubahn,² F. Faupel,⁵ M. Elbahri,^{3,4,6} and M. Bauer¹

¹*Institut für Experimentelle und Angewandte Physik, Universität Kiel, Leibnizstr. 19, 24118 Kiel, Germany*

²*Mads Clausen Institute, NanoSYD, University of Southern Denmark, Alsion 2, DK-6400 Sønderborg, Denmark*

³*Nanochemistry and Nanoengineering, Institute of Polymer Research, Helmholtz Zentrum Geesthacht, Max Planck Straße 1, 21502 Geesthacht, Germany*

⁴*Nanochemistry and Nanoengineering and* ⁵*Multicomponent Materials, Institute for Materials Science, Faculty of Engineering, Universität Kiel, Kaiserstrasse 2, 24143 Kiel, Germany*

⁶*Nanochemistry and Nanoengineering, School of Chemical Technology, Aalto University, Helsinki, Kemistintie 1, 02150 Espoo, Finland*

grossmann@physik.uni-kiel.de

An interface supporting plasmonic switching is prepared from a gold substrate coated with a polystyrene film (PS) doped with spiropheanthrooxazine (SPO). A reversible light-induced change in the surface plasmon polariton (SPP) dispersion curve of the interface is experimentally demonstrated evidencing reversible switching of surface plasmon polariton group and phase velocity [1]. The switching capabilities of the interface are furthermore successfully applied to achieve focus control of a plasmonic lens. The results imply the realization of non-volatile and reversible plasmonic switching units providing complex functionalities based on surface plasmon refraction and group delay.

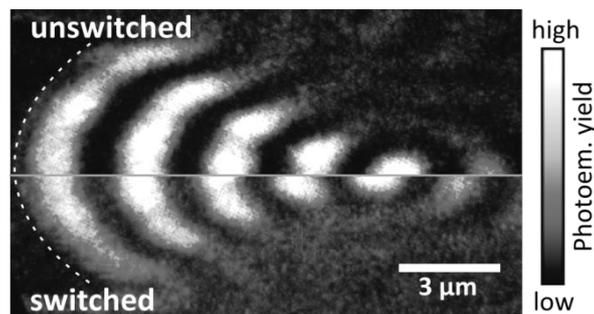


Figure 1: 2P-PEEM images of the SPP intensity pattern next to the elliptic coupling edge of a model plasmonic lens as mapped with 740 nm laser light before (unswitched) and after (switched) illumination of the PS/SPO/gold sample with UV light ($\lambda = 365$ nm); the curved periodic pattern indicates the focusing of the SPP field. A clear shift of the focal point upon switching is observable. The dashed line indicates the position of the coupling edge.

References

[1] M. Großmann, A. Klick, C. Lemke, J. Falke, M. Black, J. Fiutowski, A. J. Goszczak, E. Sobolewska, A. U. Zillohu, M. K. Hedayati, H.-G. Rubahn, F. Faupel, M. Elbahri, and M. Bauer, *ACS Photonics*, **2**, 1327–1332 (2015)

Switching of single molecules on metallic surfaces

Manuel Gruber, Richard Berndt
*Institut für Experimentelle und Angewandte Physik,
Christian-Albrechts-Universität zu Kiel, 24098 Kiel, Germany*

Molecular electronics aims at utilizing functional molecules as building blocks of electronic components. In that respect, molecules adsorbed on a surface presenting a switching functionality are particularly interesting. Such molecules are however generally fragile and the deposition of such molecules onto surfaces may result in their decomposition [1].

Molecules possessing different properties were deposited on metallic surfaces using two different techniques: sublimation for the most robust molecules and electrospray deposition [2] for the more fragile molecules. The adsorption, along with the electronic properties of the deposited molecules, were investigated using low-temperature scanning tunneling microscopy and spectroscopy. The switching of the molecules was triggered by different means, e.g. electrons, mechanical forces and adsorption of ligands, resulting in changes of molecules' properties. Indeed, the switching of molecules on surfaces can strongly affect their conformation [3], their adsorption properties [4] and/or their electronic and magnetic properties [5-7]. A strong emphasis will be given on the investigation of spin-crossover molecules, for which the switch is associated to concurrent conformational, electronic and magnetic changes [8]. Interestingly, the functionality of the molecules may initially not be present in the molecule but acquired upon adsorption on the surface.

Finally, in perspective to integration of molecules into electronic devices, the conductance through single molecules is thoroughly investigated. In particular, it will be shown that the contact geometry strongly influences the junction conductance [9].

References:

- [1] S. Karan, C. Hamann, H. Tang, A. R. Stefankiewicz, J.-M. Lehn and R. Berndt, **Chem. Phys. Chem.** **16**, 1370 (2015)
- [2] C. Hamann, R. Woltmann, I-Po Hong, N. Hauptmann, S. Karan and R. Berndt, **Rev. Sci. Instrum.** **82**, 033903 (2011)
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- [5] S. Karan, N. Li, Y. Zhang, Y. He, I-P. Hong, H. Song, J.-T. Lü, Y. Wang, L. Peng, K. Wu, G. S. Michelitsch, R. J. Maurer, K. Diller, K. Reuter, A. Weismann and R. Berndt, **Phys. Rev. Lett.** **116**, 027201 (2016)
- [6] S. Karan and R. Berndt, **Phys. Chem. Chem. Phys.** **18**, 9334 (2016)
- [7] M. Gruber and R. Berndt, **J. Phys. Chem. C** **120**, 18642 (2016)
- [8] T. Jasper-Tönnies, M. Gruber, S. Karan, H. Jacob, F. Tuczek and R. Berndt, **J. Phys. Chem. Lett.** **8**, 1569 (2017)
- [9] T. Jasper-Toennies, A. Garcia-Lekue, T. Frederiksen, S. Ulrich, R. Herges and R. Berndt, **Phys. Rev. Lett.**, accepted

A3: Spin Switching of Transition Metal Complexes

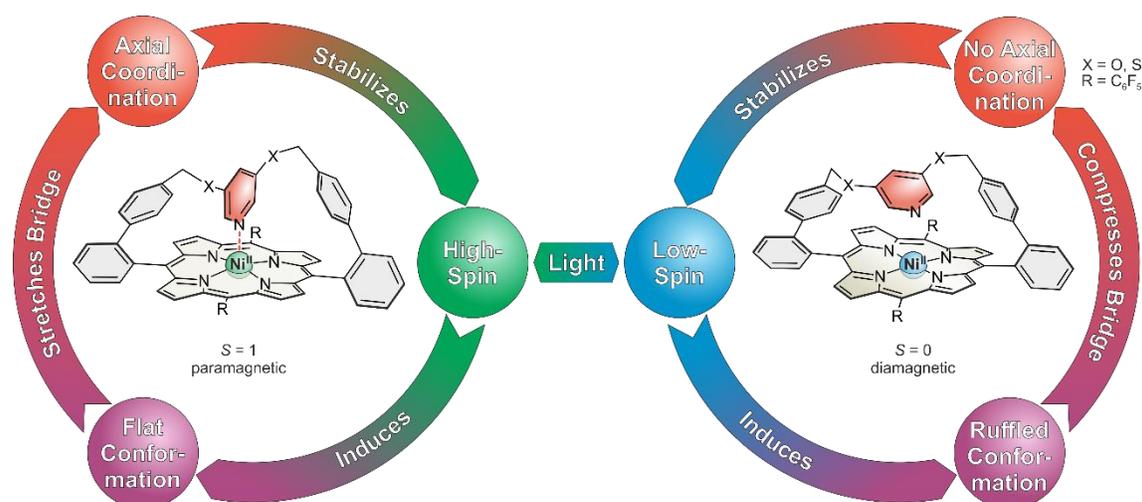
Florian Gutzeit¹, Rainer Herges¹

¹ University of Kiel, Otto-Hahn-Platz 4, 24118 Kiel, Germany

Fax: +49-431-880-1558, Tel: +49-431-880-1929; E-mail: fgutzeit@oc.uni-kiel.de

Hair clip porphyrins combine the structural change and the ligand binding affinity of photoexcited nickel porphyrins into an intramolecular feedback.^[1-3] This feedback should allow a new highly efficient photoswitching mechanism of molecular magnetic properties without utilizing photochromic groups. The rigid bridge between two *meso*-substituents prevents the intramolecular coordination of the linked ligand in the ruffled conformation of the low spin state. After photoexcitation the bridge is stretched by the flattening of the porphyrin and forces the incorporated ligand close to the nickel ion. Subsequently axial coordination occurs due to increased ligand affinity of the nickel ion in the high spin state and stabilizes the paramagnetic isomer. By excitation of the paramagnetic isomer the process should be reversible. Compared to azopyridines the intended switching mechanism requires minimal movement and does not rely on photochemical reactions like conventional photochromic switches.^[4]

Therefore switching should be feasible in solution as well as in solid state. Surface deposition is an established technique for porphyrins which extends the scope of the hair clip porphyrins. The transferability of the system between different environments opens up a variety of possible solution, surface and solid state analytics and applications.



Scheme 1. Scheme of the intramolecular feedback in Hair Clip Porphyrins towards photoswitching.

Reference

- [1] Y. Song, R. E. Haddad, S.-L. Jia, S. Hok, M. M. Olmstead, D. J. Nurco, N. E. Schore, J. Zhang, J.-G. Ma, K. M. Smith, S. Gazeau, J. Pécaut, J.-C. Marchon, C. J. Medforth, J. A. Shelnutt, *J. Am. Chem. Soc.* **2005**, *127*, 1179-1192.
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Photo-mechanizing soft matter with molecular switches

Prof. Dr. Nathalie Katsonis
University of Twente, The Netherlands

The sophistication reached by organic chemistry has enabled the design and synthesis of a wide range of dynamic molecules that display controlled shape changes with an ever-increasing refinement. However, amplifying these molecular-scale dynamics to support shape-transformation, motility, and eventually a broad range of macroscopic functions remains a key challenge. I will discuss how we draw inspiration from the operational principles of living materials in order to address this challenge, with a special focus on coupling the operation of molecular photo-switches to liquid crystal networks. Besides shape transformation and autonomous motion, we seek to pre-program adaptive mechanical properties at the macroscopic level.

Reversible photochromism in the cavities of flexible coordination cages

Dipak Samanta,^a Johannes Ahrens,^a Iddo Pinkas,^b Zonglin Chu,^a and Rafal Klajn*^a

^a Department of Organic Chemistry, Weizmann Institute of Science, Rehovot 76100, Israel

^b Department of Chemical Research Support, Weizmann Institute of Science, Rehovot 76100, Israel

E-mail: rafal.klajn@weizmann.ac.il

Placing various molecules in confined spaces can profoundly alter their physicochemical properties. Examples in nature are abundant and range from stabilizing otherwise unstable species (such as sulfenic acids¹) to orienting molecules in ways that can greatly accelerate chemical reactions between them (such as the $>10^7$ rate acceleration of CO₂ hydrolysis by carbonic anhydrase²). Over the past decade, chemists have investigated the behavior of different chemical species within synthetic confined environments. Notable examples include unusual regioselectivity and efficient catalysis of the Diels-Alder reaction within the cavities of octahedral palladium-based self-assembled cages,³ rendering white phosphorus stable to air,⁴ and promoting cationic reaction cascades leading to efficient terpene cyclizations.⁵ Inspired by the fascinating process of retinal photoisomerization within the cavity of rhodopsin,⁶ we are broadly interested in the behavior of photoswitchable molecules under confinement.⁷⁻¹⁰ Here, I will present our latest studies on the encapsulation of photoswitchable molecules within flexible self-assembled cages based on imidazole-palladium coordination. We found that the uptake of spiropyran by our cages is accompanied by its isomerization to its otherwise unstable, ring-open (merocyanine) form. The reaction proceeds quantitatively even for spiropyran lacking the nitro group typically used to stabilize the open form. The encapsulation renders spiropyran responsive to blue light, and the light-induced ring closing/spontaneous (dark) ring opening sequence can be repeated multiple times. This unexpected behavior of spiropyran within the cavities of these cages enabled us to fabricate gels, in which images could be created with light. Moreover, we found that a spontaneous conversion of the merocyanine form (blue) to the protonated merocyanine form (faint yellow) occurred spontaneously upon the dehydration of the system. This finding inspired us to prepare paper in which writing can be performed with water as the ink. We have also demonstrated an efficient uptake of various azobenzenes using the same flexible cages. Interestingly, azobenzene molecules were encapsulated as dimers, as confirmed by X-ray crystallography. This observation paves the way to studying the photoswitching behavior of discrete oligomers of photoswitchable molecules (here, dimers) within confined spaces.

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**Function by Switching:
Molecular Assemblers, Molecular Machines Performing
Synthesis)**

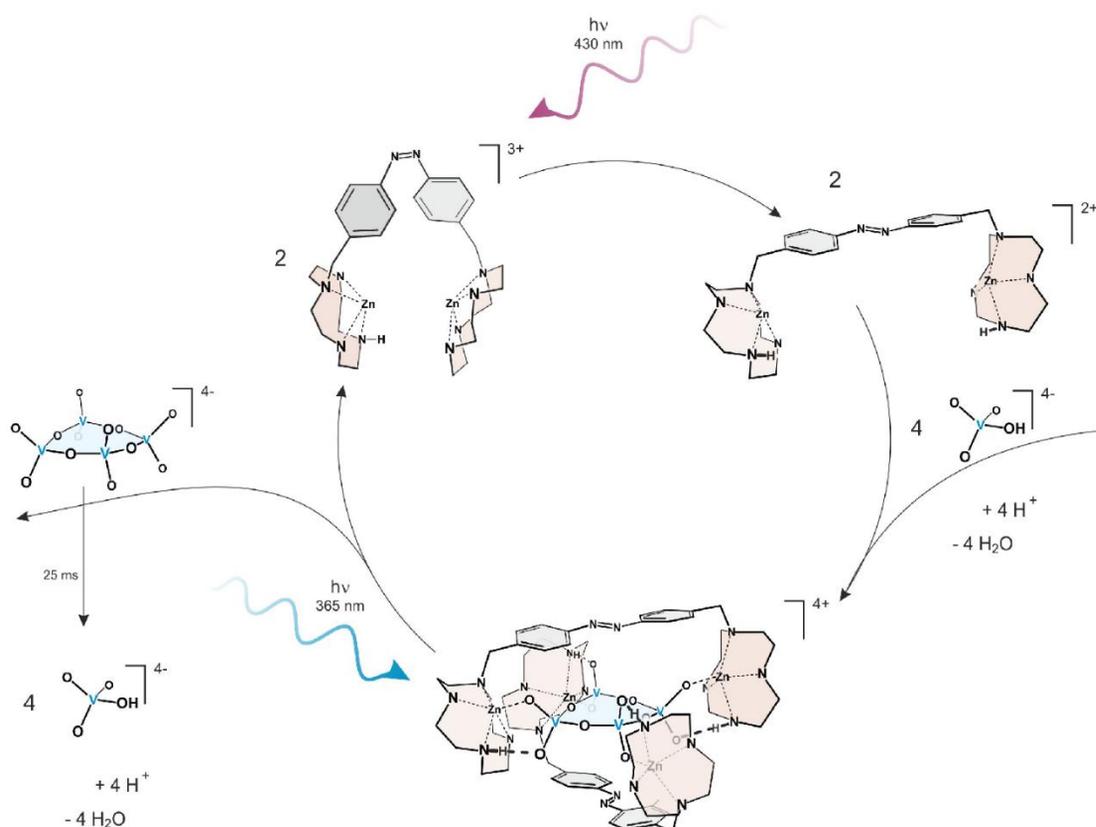
Rainer Herges

Otto-Diels-Institute for Organic Chemistry, Kiel University, Germany

rherges@oc.uni-kiel.de



In chemical synthesis usually the reactants are dissolved in an organic solvent, the reactive molecules undergo stochastic collisions and form a bond if kinetic energy and relative orientation are favourable. However, the majority of biologically active molecules in nature are synthesized in ATP driven, molecular machine-type enzyme complexes such as non-ribosomal peptide synthetases (NRPS) or polyketide synthases (PKS). They operate like an assembly line by guiding reactions under positioning control driven by ATP. Notwithstanding the fact that there are a number of advantages to this assembler-like synthesis (less side reactions, easy stereo control, no protecting groups, preselection of reactants, driving unfavourable reactions...), there is (according to the best of our knowledge) no artificial system published so far. We are aiming at the design, synthesis and investigation of the first model system of a molecular assembler. In our preliminary work we designed and synthesized a light-switchable ditopic receptor which is able to drive the condensation of 4 molecules of vanadate to a cyclic tetravanadate. The reaction which is endergonic and therefore not spontaneous in the absence of the ligand is driven by the large and selective binding energy of the product tetravanadate inside the receptor. Photochemical isomerization (365 nm) of the ligand releases the product. Upon irradiation with 430 nm the original, "empty" state is restored and the cycle starts again.



Vibrationally coherent optomechanical energy transduction in biomimetic molecular switches.

Moussa Gueye,¹ Massimo Olivucci,^{1,2} Stefan Haacke,¹ Jérémie Léonard¹

¹*Université de Strasbourg, CNRS, Institut de Physique et Chimie des Matériaux de Strasbourg, F-67034 Strasbourg, France*

²*Dipartimento di Biotecnologie, Chimica e Farmacia, Università di Siena, Italy & Chemistry Department, & Bowling Green State University, Ohio, United States*

E-mail: Jeremie.Leonard@ipcms.unistra.fr

Ultrafast C=C double bond photoisomerization converts light energy in mechanical energy at the molecular scale and may therefore be exploited in molecular devices for functional switching or rotary motion.[1] In the rhodopsin protein (Rh), the sensor for vision, the ultrafast photoisomerization of the protonated Schiff base of retinal (PSBR) triggers the protein activity. This photoreaction has outstanding speed and quantum yield and it appears to be vibrationally coherent, meaning that the energy of the absorbed photon is efficiently funneled into the isomerization coordinate on a time scale faster than energy dissipation to the environment. This unique property is the promise for an optimum photomechanical energy conversion. Following a biomimetic approach, the N-alkylated indanylidene-pyrrolinium (NAIP) molecular framework (see Figure 1A) was designed and synthesized such that its π -electron system would mimic that of PSBR in Rh. Consequently, its photoreaction dynamics in solution was shown to be very similar to that of Rh [2], including signatures of low-frequency vibrational coherence in the photoproduct ground state[3].

Here we apply a recently built experimental set-up utilizing sub-8fs UV-vis pulses to perform vibrational coherence spectroscopy [4] on the NAIP compounds. The objective is to reveal the signatures of the vibrational dynamics that drives the system through the conical intersection from the initial (Franck Condon) structure to the photoproduct. Importantly, the vibrational activity and photoreaction dynamics are critically influenced by the intramolecular steric hindrance imposed by a simple methyl substitution. Hence, we demonstrate that the appropriate chemical design may turn on or off this vibrationally coherent mechanism in the NAIP compounds. Computational quantum chemistry allows us to rationalize the underlying steric-electronic effect. We discuss the possible implications of this finding on the mechanism engineered by Rh to enhance the retinal isomerization yield, and on the future design of synthetic molecular switches targeting enhanced photoreaction yield.

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Ultrafast multidimensional spectroscopy of charge-transfer processes in light-harvesting systems

Christoph Lienau^{1,2*}

¹ *Institute of Physics, Carl von Ossietzky University Oldenburg, 26129 Oldenburg, Germany,*

E-mail address: Christoph.lienau@uni-oldenburg.de

The efficient conversion of (sun-)light into electrical or chemical energy is one of the most fundamental processes in biology and at the same time a highly-relevant challenge in current energy research. Generally, it is well understood that the underlying microscopic conversion processes happen on an exceedingly short femtosecond time scale and typically involve the transfer of charge from an optically bright donor moiety to an optically dark acceptor system. What is less clear is whether vibronic quantum coherence is helpful or maybe even necessary for those processes to occur and to what extent vibronic quantum coherence modifies the transport of charges through these systems. In my talk, I want to give a few examples how ultrafast, two- and three-dimensional optical spectroscopy – combined with advanced theoretical modelling - can shed new light on those questions how it can provide quite detailed insight into quantum-coherent photoinduced charge separation processes [1-3]. Specifically, I want to discuss the possible role of conical intersections on these processes.

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Functionalization and Investigation of Azo Functionalized TATA Platforms

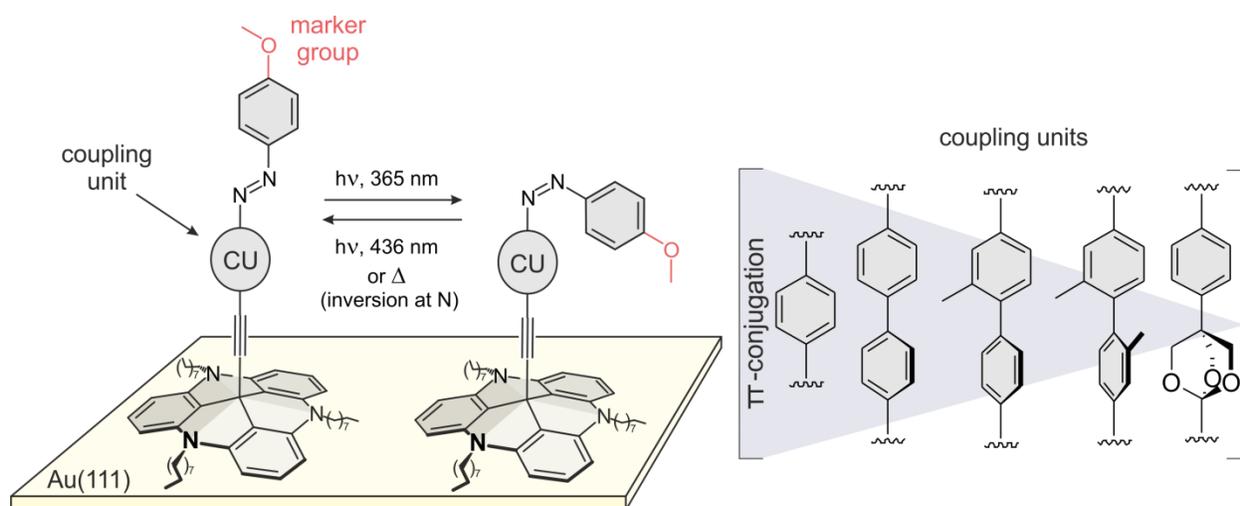
R. Löw¹, T. Rusch², A. Schlimm³, R. Herges¹, O. Magnussen², F. Tuczek³

¹Otto Diels-Institute of Organic Chemistry, Christiana-Albertina-University, Otto-Hahn-Platz 4, 24118 Kiel, Germany, E-mail: rloew@oc.uni-kiel.de

²Institute of Experimental and Applied Physics, Christiana-Albertina-University, Leibnizstraße 19, 24118 Kiel, Germany, E-Mail: rusch@physik.uni-kiel.de

³Institute of Inorganic Chemistry, Christiana-Albertina-University, Max-Eyth-Straße 2, 24118 Kiel, Germany, E-mail: aschlimm@ac.uni-kiel.de

Upon irradiation with UV light (~365 nm) azobenzenes isomerize from their *trans* configurations to the corresponding *cis* isomers. The reaction back to the more stable *trans* isomer can either be performed by irradiation with visible light (~430 nm), or it proceeds spontaneously in the ground state. In homogeneous solution, the thermal *cis* to *trans* isomerization is slow at room temperature with half-lives of hours to days. The half-life of the parent azobenzene is 5 days at 25°C in benzene.¹ Similar values have been determined in other solvents, in the gas phase and in the melt.² Very surprisingly, we observed half-lives of azobenzenes that are three orders of magnitudes faster (less than a minute) if the azobenzenes are connected via an ethyne spacer to a molecular platform which is absorbed on a Au(111) surface (see illustration). Since there is π conjugation from the azobenzene through the triple bond into the π system of the platform, we attributed this more than 1000fold rate acceleration to some unknown effect which is related to electronic coupling to the surface. To check this hypothesis, we gradually reduced π conjugation by systematic variation of the spacer. Biphenyls are known to exhibit decreasing conjugation with increasing torsional angle between the two phenyl rings. This torsional angle in turn can be increased by introducing substituents in *ortho* position of the biphenyl unit. If conjugation is completely shut off (e.g. with two methyl groups) the *cis-trans* isomerization rate is almost the same in solution and on the surface confirming our preliminary hypothesis.



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Transformation of an Iron(II) Cage from High- to Low-Spin Switches Guest Release in a Two Cage System

Anna McConnell,^{a, b} Catherine Aitchison,^a Angela Grommet^a and Jonathan Nitschke^a

^a Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, UK

^b Otto Diels Institute of Organic Chemistry, Christian-Albrechts-Universität zu Kiel, Otto-Hahn-Platz 4, D- 24098, Germany

Metal-organic cages function as molecular containers as there is the potential to encapsulate guests with high affinity and selectivity within their well-defined cavities.¹ Subcomponent self-assembly exploits the reversible formation of covalent and coordinative bonds to prepare metal-organic cages from relatively simple subcomponents. A wide variety of architectures from tetrahedra to icosahedra can be self-assembled through the formation of imine bonds around metal centres. There is growing interest in stimuli-responsive cages, whose properties (e.g. guest uptake/release) are altered in response to an external signal, in order to construct molecular networks approaching the complexity and functionality exhibited by signalling pathways in biological systems.² We report spin state switching of a cage as a new strategy for signal transduction; the transformation of a high-spin Fe^{II}L₄ cage to its low-spin analogue is exploited to switch guest release in a two cage system.³

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Structure and Kinetics of Switching in Phospholipid Membranes

Bridget Murphy

Having integrated Amphiphilic photoswitchable molecules into phospholipid membranes, we investigate their biologically relevant properties. By studying the interactions in such a model system consisting of switchable biomimetic molecules in lipid membranes here, we study the structure and kinetics of membrane response to the switching process. These *in situ* experiments not only contribute to the fundamental understanding of membrane dynamics but also will contribute to potential applications for molecular switches such as drug delivery. 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). This allows us to reversibly change the azobenzene-glycolipid orientation between trans- and cis-conformation by illumination with UV and blue light. We have followed the structural changes in this model membrane and the switching kinetics of the system with Langmuir isotherms and *in situ* X-ray methods, X-ray reflectivity and grazing incidence diffraction. The membrane structure responds on a time scale of seconds upon UV illumination. Switching from trans to cis conformation results in changes in molecule tilt and spacing and also membrane thickness. A critical point in surface pressure at 18.4 mN/m has been discovered above which the membrane expands rather than compresses upon switching from trans- to cis- conformation.

Photoswitching of Bacterial Adhesion

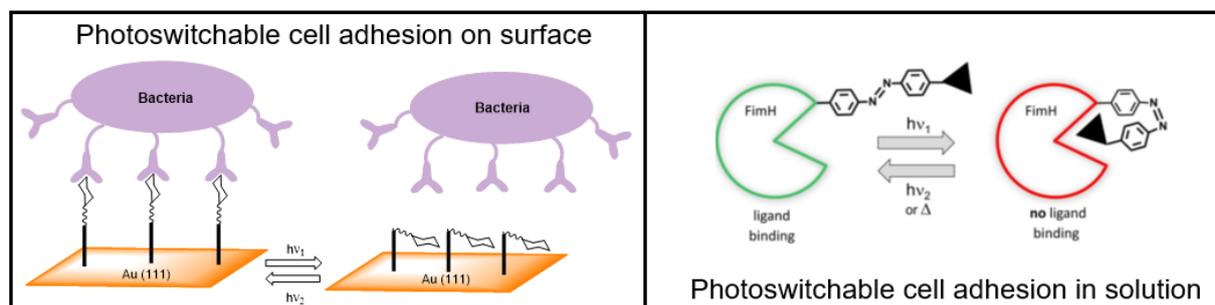
Vivek Poonthiyil, Thisbe K. Lindhorst

E-mail: vpoonthiyil@oc.uni-kiel.de / tklind@oc.uni-kiel.de

Otto Diels Institute of Organic Chemistry, Christiana Albertina University of Kiel,
Otto-Hahn-Platz 3/4, 24098 Kiel, Germany

Glycocalyx, the carbohydrate-rich layer lining the outermost part of the endothelium, is one of the most important and intriguing surfaces in biology. Molecular interactions between glycocalyx components and the carbohydrate-specific proteins (lectins) initiate multiple biological functions such as cell adhesion, immune response, and cell signaling. 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. The aim of our project is to accomplish photoswitching of bacterial cell adhesion. With selective photoswitching of carbohydrate-specific bacterial adhesion, we aim to differentiate “good” (own) and “bad” (alien) cell adhesion with temporal and spatial resolution.

So far, we have synthesized and studied mono- and disaccharide azobenzene glycosides and investigated the influence of sugar configuration and azobenzene substitution on their photochromic properties.^{1,2} Furthermore, we have synthesized many multivalent azobenzene glycosides and have also shown how the versatile “click” chemistry can be used for this purpose.³ Our studies on the inhibitory potential of azobenzene mannosides in bacterial adhesion (*E. coli* with type 1 fimbriae, which possess an α -D-mannoside-specific lectin named FimH in its terminus) show that they are potent ligands of FimH.¹ Also, azobenzene mannosides with *E* or *Z* configuration bind approximately equally well to FimH, regardless of the configuration of the azobenzene N=N double bond. As a highlight of our project, we have successfully prepared photoswitchable SAMs (self-assembled monolayers) of azobenzene glycosides on gold surface.⁴ With these SAMs we have shown, for the first time, that three-dimensional presentation of carbohydrates is critical in their interaction with bacteria.⁵ We found that when *E* azobenzene-conjugated mannoside derivatives on the gold surface were photoswitched to the *Z* form, the number of adherent bacteria (*E. coli* with type 1 fimbriae) decreased by a factor of five. We have also demonstrated that the carbohydrate-orientation based bacterial adhesion results are valid when azobenzene mannosides were immobilized on the surface of human cells too.⁶



Currently, we are trying to improve photoswitching on surfaces and also to understand the structure-function relationships that underlie the observed biological effects. To that end, we plan to prepare “self-diluting” systems with molecules that occupy space during the assembly process, which can, in a consecutive step, be released by cleavage “on SAM”. Also, we will synthesise azobenzene glycoclusters, which will permit to differentiate the effect of “scaffolded multivalency” from “surface-based” multivalency. In another approach towards better photoswitchable glycoarrays we plan to use a concerted “enforced” *E/Z* isomerization of glyco-

SAMs with molecules possessing a rigid backbone.¹ Finally, in order to explore the effect of carbohydrate orientation in bacterial adhesion in a relatively complex glyco-SAMs, we will prepare mixed SAMs with two different types of azobenzene glycosides. The two ligands will be chosen in such a way that they undergo photoisomerization under different wavelengths and adhere to *E.coli* strains with different carbohydrate specificity. These orthogonal glyco-SAMs will be a better mimic of glycocalyx and will take us a step closer towards understanding the functioning of glycocalyx.

On another front, in order to achieve photoswitching of bacterial adhesion in solution, the adhesive protein FimH will be modified site-specifically to make ligand binding switchable by reversible blocking of the carbohydrate binding site of the lectin. Modification of the protein FimH shall result in installation of a photoswitchable azobenzene derivative to act as a “gate keeper” molecule for reversible blocking of the entrance of the lectin’s carbohydrate binding site. This will allow photoswitching of bacterial adhesion in solution, independently of a modified surface. Our studies on photoswitching of bacterial adhesion both on glyco-SAMs and in solution will provide a better understanding of the bacterial adhesion mechanism along with shedding more light into the functioning of glycocalyx.

Acknowledgement: Our collaborations with the Tucek (Kiel) and the Terfort (Frankfurt) groups are gratefully acknowledged.

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Covalently Linked Magnetic Complexes on Surfaces: Spin Delivery, Logic Devices and Photo-Switches

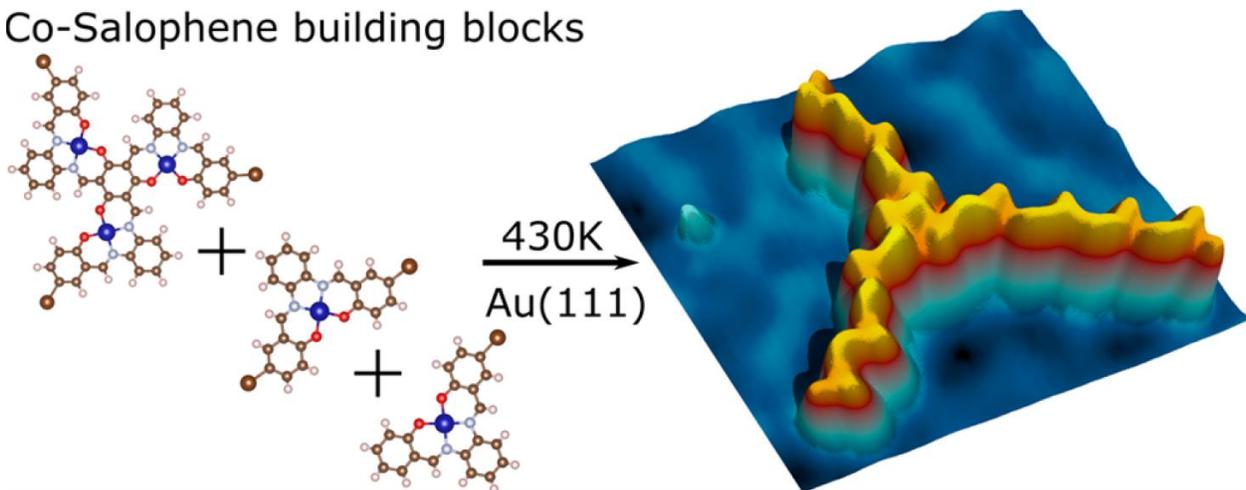
Marc Heinrich Prosenc,^{a,b} Bernhard E. C. Bugenhagen^a, Annika G. Frank^a

a) Universität Hamburg, Martin-Luther-King-Platz 6, D-20146 Hamburg

b) Present address: TU Kaiserslautern, Department of Chemistry, Erwin-Schrödinger-Strasse 52, D-67663 Kaiserslautern

Molecular spintronic devices offer great potential for future energy-efficient information technology as they combine ultimately small size, high-speed operation, and low-power consumption. Recently, atom by-atom assembly together with spin-sensitive imaging and characterization at the atomic level have led to a first prototype of an all-spin atomic-scale logic device [1]. One major disadvantages of such atom based spintronic device is its low thermal stability of the assembly. By employing tailor-made paramagnetic molecular building blocks, combined with deposition under ultra-high vacuum conditions as well as surface chemistry[2], a corresponding prototype of an all-spin based molecular device can be realized.

Co-Salophene building blocks



Such molecular device concepts offer the advantage of inherent parallel fabrication based on molecular self-assembly as well as considerably higher operation temperatures due to enhanced energy scales of covalent through-bond linkage of basic molecular units compared to substrate-mediated coupling schemes employing indirect exchange coupling between individual adsorbed atoms on surfaces. Further advantages are, that the molecular end electronic properties of the molecules remain which extend the scope of molecular based devices.

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NEXAFS study of novel robust spin crossover films on metallic surfaces

Sebastian Rohlf¹, Benedikt Flöser², Matthias Kalläne, Simon Jarausch¹, Felix Tuczek², and Kai Rossnagel¹

¹*Institute of Experimental and Applied Physics, Kiel University, Leibnizstraße 19, 24118 Kiel, Germany*

²*Institute of Inorganic Chemistry, Kiel University, Max-Eyth-Straße 2, 24118 Kiel, Germany*

The spin-state manipulation of Fe(II) coordination complexes by external stimuli is associated with a change in the electronic, magnetic, and structural properties. In particular, the temperature- and light-induced switching mechanisms may be utilized in future spintronic devices. Both of these switching effects were observed even in single monolayers adsorbed on the weakly interacting substrate HOPG^[1]. Nevertheless, the dissociation of spin-crossover (SCO) molecules in direct contact to a metal surface is still impeding measurements in device-like environments. A novel approach to overcome this limitation is the electronically stabilized SCO system Fe(PyPyr(CF₃)₂)₂(phen), a recently synthesized derivative of the well-studied complex Fe(H₂B(pz)₂)₂(phen)^[2,3].

Here, we present near edge X-ray absorption fine structure (NEXAFS) spectroscopy results of ultrathin films of Fe(PyPyr(CF₃)₂)₂(phen) adsorbed on Au(111) and TiTe₂, for different temperatures and laser light irradiation conditions. Our results confirm a complete and reversible light-induced spin-crossover in thin films of this derivative, prepared under ultra-high vacuum conditions.

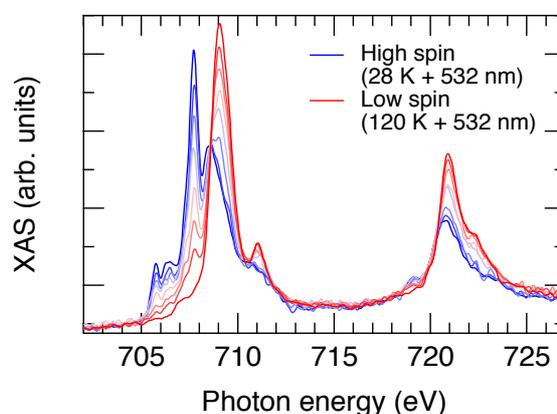


Fig. 1: Fe-L-NEXAFS spectra of Fe(PyPyr(CF₃)₂)₂(phen) on TiTe₂ at various temperatures during 532 nm laser light irradiation.

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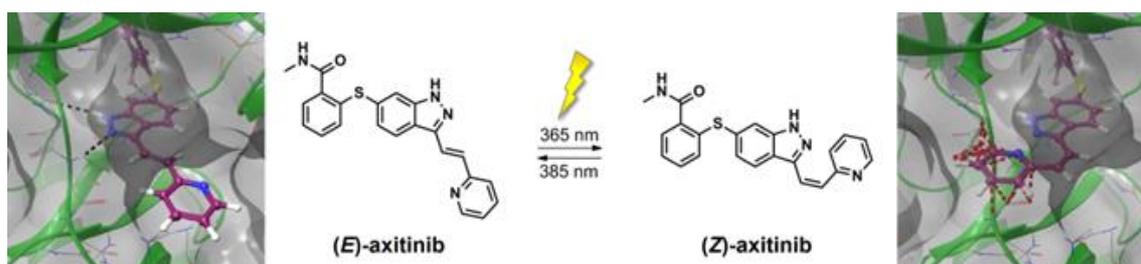
A Photoswitchable Kinase Inhibitor: Photoinduced *E/Z* Isomerization of Axitinib

Dorian Schmidt,¹ Linda Heintze,¹ Theo Rodat,¹ Rebecca Horbert,¹ Jantje Weber,¹
Christian Renn,¹ Boris Pinchuk,¹ Christian Peifer^{1,*}

¹*Institute of Pharmaceutical Chemistry, University of Kiel, Kiel, 24118, Germany*
E-mail: dschmidt@pharmazie.uni-kiel.de, cpeifer@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 drug targets and the development of small molecule kinase inhibitors has become a major field in pharmaceutical research. [1]

Our goal is to develop photoswitchable kinase inhibitors that can be spatially and temporally controlled by light. These compounds will be useful not only for innovative therapeutic approaches but also as novel pharmacological tools, e.g. for resolving dynamic aspects of kinase signal transduction.



Scheme 1. (Left): (*E*)-axitinib in the ATP binding pocket of VEGFR2 (pdb code 4AG8). [2]. (Right): Superposition with (*Z*)-axitinib (steric clashes with the protein are indicated as red dotted lines).

In the present study, we focused on the protein kinase inhibitor axitinib which is approved for advanced metastatic renal cell carcinoma (RCC) since 2012. Interestingly, axitinib undergoes an *E-Z* isomerization upon irradiation with UV light (Scheme 1). [3] Hence, our goal was to explore if its inhibitory effect can be turned “on” and “off” triggered by light.

Indeed, we could demonstrate that (*Z*)-axitinib is up to 43 times less active in an *in vitro* VEGFR kinase assays and 19 times less active on human umbilical vein endothelial cells (HUVEC) compared to (*E*)-axitinib. By irradiating (*Z*)-axitinib with UV light (385 nm) it is possible to switch it completely to the (*E*)-isomer and to restore the biological activity of (*E*)-axitinib. However, *vice versa* it is not possible to switch the biological activity of (*E*)-axitinib “off” in aqueous solution.

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Orbital Imaging by Angle Resolved Photoelectron Spectroscopy: From Basic Principles to High Resolution Experiments and Limitations

Achim Schöll

Universität Würzburg, Experimentelle Physik VII, 97074 Würzburg, Germany

E-mail: achim.schoell@physik.uni-wuerzburg.de

In recent years angle-resolved photoelectron spectroscopy (ARPES) has emerged as a particularly powerful tool for the imaging of orbitals [1,2]. In this talk I will briefly introduce this technique and discuss its prospects and main limitations.

The imaging of orbitals in momentum space by ARPES has been applied in several instances, e.g. to show hybridization at interfaces [3], the resulting band dispersion [4] and many particle effects [5,6]. By retrieval of the phase information, which can be done by mathematical algorithms [7] or by experiments with circular light polarization [8] orbitals can also be reconstructed in real space and in three dimensions [9].

In particular by using state-of-the-art momentum microscopes with high energy resolution in combination with synchrotron radiation orbital imaging by ARPES can provide unprecedented insight into the properties of molecular materials. For example, photoelectron momentum microscopy with high energy resolution allows imaging of molecular orbitals with resolution of vibronic modes. I will demonstrate that the intensity patterns of photoelectrons derived for the vibronic sidebands of molecular states show characteristic changes due to the distortion of the molecular frame in the vibronically excited state (see Figure 1). By a comparison to the simulated patterns derived from calculations, an assignment of the specific vibronic mode that preferentially couples to the electronic excitation is possible, which in the example of the highest occupied molecular orbital (HOMO) of coronene is a b_{2u} inplane mode with an energy of 0.2 eV [10]. Orbital imaging by photoelectron momentum mapping with vibronic resolution thus provides unique information for the analysis of the coupling between electronic and vibronic excitation.

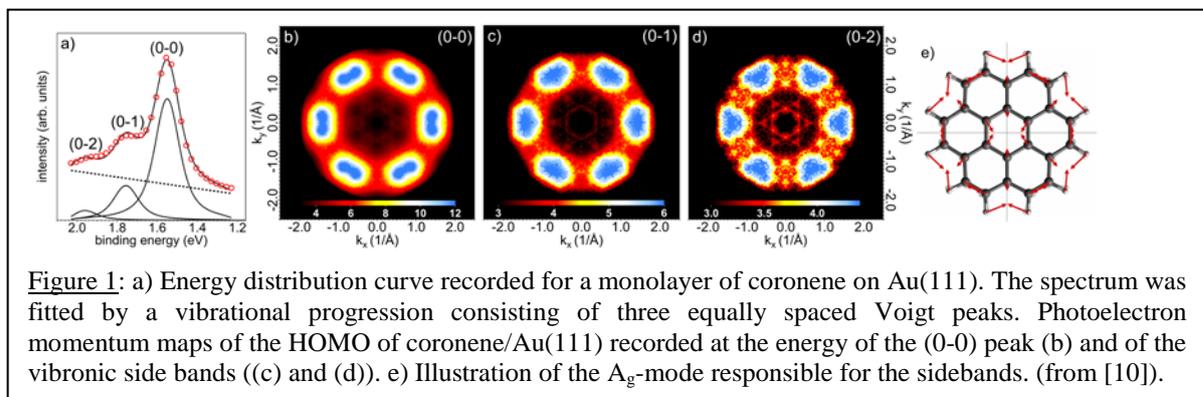


Figure 1: a) Energy distribution curve recorded for a monolayer of coronene on Au(111). The spectrum was fitted by a vibrational progression consisting of three equally spaced Voigt peaks. Photoelectron momentum maps of the HOMO of coronene/Au(111) recorded at the energy of the (0-0) peak (b) and of the vibronic side bands ((c) and (d)). e) Illustration of the A_g -mode responsible for the sidebands. (from [10]).

Limitations of the technique are mainly imposed by the plane wave final state approximations. As I will demonstrate, this is not sufficient for certain experimental conditions, three dimensional objects, or if scattering cannot be neglected. In such cases more elaborated calculations such as time-dependent DFT [11] or the Independent Atomic Center approximation can provide a more exact description of the ARPES data.

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Polymer Composite Inspired by the Human Skin: Molecular Switches in Complex Environments

Progress Report on Mechanophoric Composites

Sindu Shree¹, Mathias Schulz-Senft,² Ruchira Pereira,² Leonard Siebert,¹ Anne Staubitz^{2,3}, Rainer Adelung¹

¹*Institute for Materials Science, Functional Nanomaterials, University of Kiel, Kaiserstr. 2, 24143 Kiel, Germany*

²*Otto-Diels-Institute for Organic Chemistry, University of Kiel, Otto-Hahn-Platz 4, 24118 Kiel, Germany*

³*Institute for Organic and Analytical Chemistry, University of Bremen, Leobener Str. NW2 C, 28359 Bremen, Germany*

Molecular switches such as azobenzene, spiropyran and spirooxazine have been incorporated into several complex environments for example azobenzene in liquid crystalline polymer for a photo-mechanical effect and spiropyran in polymer chains as a multi-stimuli component. Here presented is a research on direct and indirect incorporation of the molecular switches in various polymers. Spiropyran and spirooxazine were used as fillers; by simply dispersing it into the chemically stable and solvent free polythiourethane (PTU) multi-stimuli composites were produced. A very efficient UV sensor existing in the nature is human skin. Inspired by the human skin a polymer composite based on a photochromic spirooxazine is part of the presented work. Molecular switches used here are the molecules that undergo a well known spiro-mero reversible isomerisation under UV light indicated by a color change. The isomerisation is reversed either by visible light or by thermal relaxation. When the photochromic polymer composite was exposed to the direct sunlight it turned purple. The PTU/spirooxazine composite was then partially covered with a sunscreen spray (SPF 50+) and was placed under sunlight. As the sunscreen fade the exposed colorless polymer composite turns purple as shown in the figure 1. An objective of the project C-14 was to covalently integrated spiropyran into the polymeric chains of polymethylacrylate (PMA), polymethylmethacrylat (PMMA) which was later coated around the glass fibers and T-ZnO to enhance the mechanical stability of the matrix and to obtain a self-reporting mechanophoric composite. Mutli-stimuli fibers were produced by spinning the polymer PMA-SP-PMA with the help of a self-made centrifugal spinner.

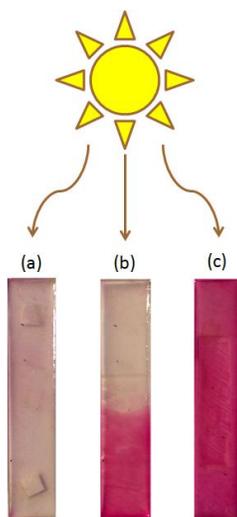


Figure 1: Images of a photochromic polymer composite undergoing reversible isomerization when exposed to sunlight. (a) The PTU/photochrome composite completely covered with a sunscreen spray under the sunlight. (b) The composite partially covered with a sunscreen spray under sunlight. (c) The composite without sun protection under the sunlight.

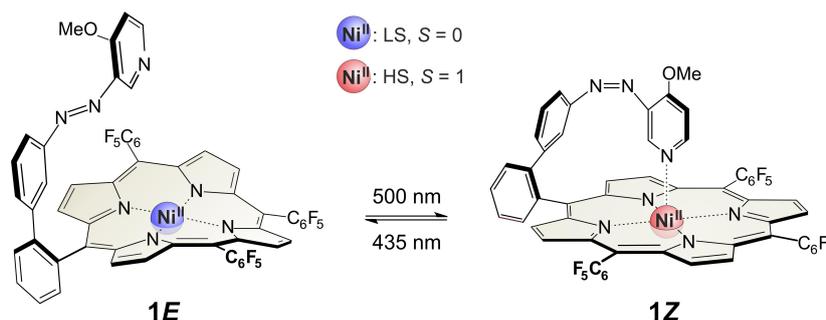
Ultrafast Photo-induced Dynamics of the Magnetically Bistable Azopyridine/Ni-Porphyrin Record Player Spin Switch

S. Megow¹, J. Bahrenburg¹, H. Bhnke¹, M. Bohnsack¹, M. Dittner¹, B. Kohly,¹ J. Gripp,¹ D. Bank,¹ R. Marschan,¹ M. Dommaschk², C. Schtt², R. Herges², F. Temps¹

¹ Institute of Physical Chemistry, Christian-Albrechts-University Kiel

² Institute of Organic Chemistry, Christian-Albrechts-University Kiel

The azopyridine-functionalized Ni-porphyrin **1** [Venkataramani et al., Science **2011**, 331, 445; Fig. 1] shows magnetic bistability in homogeneous solution at room temperature. On irradiation at $\lambda \sim 500$ nm, the four-coordinate low-spin (LS) Ni switches to its high-spin (HS) state, which is stabilized by axial coordination of the azopyridine ligand that undergoes *trans*-to-*cis* (*E*-to-*Z*) isomerization. At $\lambda \sim 435$ nm, this process is reversed and the LS state is efficiently recovered.



We have investigated the ultrafast dynamics of the *E*-LS and *Z*-HS states of **1** using femtosecond transient electronic absorption spectroscopy after photoexcitation in the Q band or in the B band of the porphyrin. The four-coordinate *E*-LS species **1E** was found to exhibit virtually identical dynamics as the plain Ni-porphyrin. Transient switching to the LS state happens in <0.25 ps, but *E*-to-*Z* isomerization of the azopyridine arm and stabilization of the HS state in the form of **1Z** is very inefficient, making this a very minor channel. The five-coordinate *Z*-HS compound **1Z**, on the other hand, also shows virtually immediate spin switching in <0.25 ps, subsequent vibrational cooling in ~ 12 ps, followed by a persistent weak residual LS product absorption lasting beyond $\Delta t = 1$ ns. The measured quantum yields are, however, very low ($\Phi_{\text{HS} \rightarrow \text{LS}} = 0.06 - 0.01$, $\Phi_{\text{1Z} \rightarrow \text{1E}} = 0.02 - 0.03$; vs. $\Phi_{\text{1E} \rightarrow \text{1Z}} < 0.01$). The photo-induced dynamics are dominated by coupling of the porphyrin $\pi\pi^*$ and Ni(d-d)/Ni(d²) states, not by initial photo-isomerization of the azopyridine. The very minor *Z*-*E* isomerization of the ligand might instead take place via the azopyridine triplet state.

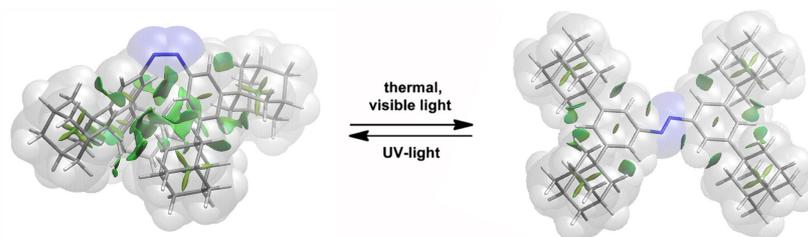
ABSTRACT

Azobenzene switches – from physical organic chemistry to energy storage

Prof. Dr. Hermann A. Wegner, Justus-Liebig-Universität, Gießen, Germany

The synthesis and control of structure on the molecular level allows designing properties to address fundamental questions in chemistry and to develop new materials.

Azobenzene switches have been applied extensively to control functionality on the molecular level. However, the understanding of the switching processes is still an active field of research. The incorporation of azo units within macrocycles, for instance, allows to probing their inherent properties. Additionally, azobenzene switches have been applied to investigate one of the most basic interactions in chemistry - the attractive London-dispersion as part of the van-der-Waals forces. Finally, the potential for materials applications is discussed.



Angew. Chem. Int. Ed., **2015**, *54*, 13436-13439. *Org. Biomol. Chem.* **2014**, *12*, 3371.

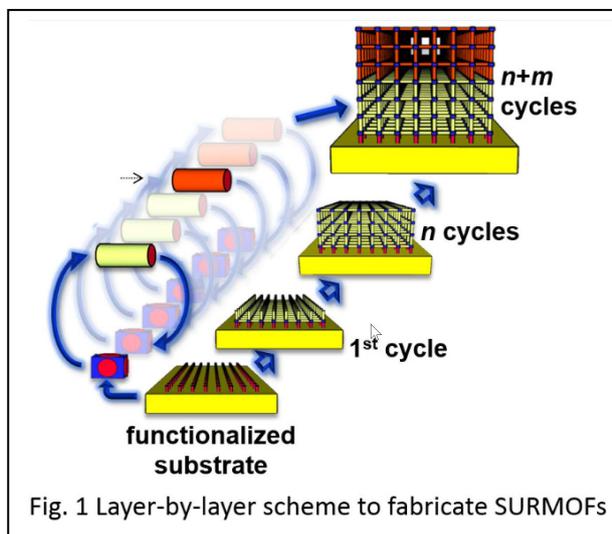
Liquid Phase Epitaxy of Molecular Frameworks on Solid Substrates: A New Class of Designer Solids?

Christof Wöll

Institute of Functional Interfaces (IFG), Karlsruhe Institute of Technology, FRG

With regard to the development of approaches to realize “Designer Solids” by programmed assembly of building units taken from libraries, recently metal-organic frameworks (MOFs) have attracted a huge interest. Here, we will focus on MOF-based electrochemical [1,2], photoelectrochemical [3] and photovoltaic devices [4,5]. Internal interfaces in MOF heterostructures are also of interest with regard to photon-upconversion [6] and can be used for the crosslinking of sandwiched, reactive monomers [7]. Since the fabrication of reliable and reproducible contacts to MOF-materials represent a major challenge, we

have developed a layer-by-layer (lbl) deposition method to produce well-defined, highly oriented and monolithic MOF thin films (SURMOFs) on a number of different substrates.



At present, the whole field is reaching a rather mature state, with a number of functioning SURMOF-based devices, and many other proposed [10]. In the talk, we will present a few examples to demonstrate the state of the art and the main challenges. Furthermore, we will discuss the potential of these „Designer Solids“ to construct host matrices for studying molecular interactions, and in particular the switching of photoactive compounds.

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ABSTRACTS FOR POSTERS

in alphabetical order of presenters

Ultrafast photoisomerization dynamics of heterodiazocines upon $S_1(n\pi^*)$ photoexcitation by femtosecond electronic absorption spectroscopy

Dennis Bank¹, Ronja Höppner¹, Melanie Hammerich², Falk Renth¹, Bernd Hartke¹, Rainer Herges², and Friedrich Temps¹

¹*Institute of Physical Chemistry, Christian-Albrechts-University Kiel, Olshausenstr. 40, D-24118 Kiel, Germany*

²*Institute of Organic Chemistry, Christian-Albrechts-University Kiel, Olshausenstr. 40, D-24118 Kiel, Germany*

E-mail: bank@phc.uni-kiel.de

Diazocines are bridged azobenzenes which exhibit much higher switching efficiencies and quantum yields than normal azobenzenes.^[1,2] Chemical substitution of the chain enables a high

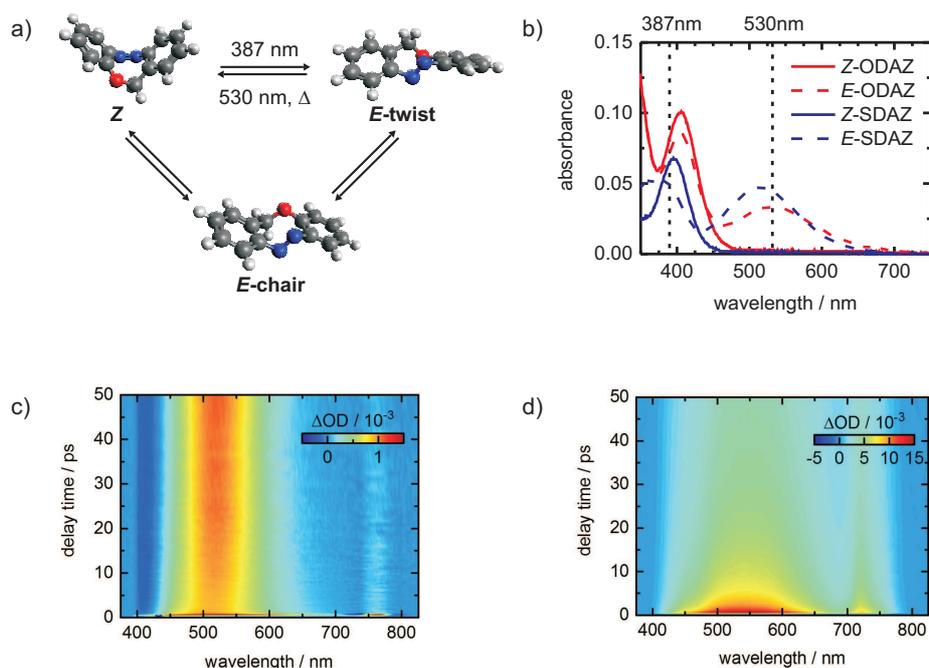


Figure 1: a) Photoisomerization scheme of ODAZ. The thermodynamically stable E-form and the two possible Z-isomers after photoexcitation are shown. b) Static UV/vis spectra of the E-isomers and Z-isomers of ODAZ and SDAZ. Two-dimensional spectro-temporal absorption maps of c) ODAZ and d) SDAZ after $S_1(n\pi^*)$ excitation at 387 nm.

variation potential. Depending on the heteroatom incorporated in the bridge moiety, the photochemical behavior changes dramatically.

We investigated 12*H*-dibenzo[*b,f*][1,4,5]oxadiazocine (ODAZ)^[3] and 12*H*-dibenzo[*b,f*][1,4,5]thiadiazocine (SDAZ)^[3] using femtosecond time-resolved electronic absorption spectroscopy. The *Z* → *E* isomerization of both components was studied after excitation at $\lambda = 387$ nm and probed at wavelengths from $\lambda = 390 - 750$ nm. The observed transient spectra for ODAZ show an initial intense excited-state absorption (ESA) which decreases within the experimental time resolution ($\tau < 150$ fs). After $\Delta t = 10$ ps a positive contribution grows in which can be assigned to product formation. Additionally, we observed a ground state bleach below $\lambda = 400$ nm. These ultrafast dynamics are confirmed by quantum chemical calculations employing a floating occupation configuration-interaction (FOCI-AM1) method. In contrast, SDAZ shows much slower dynamics. A strong ESA band was observed dominating the spectral signature over the entire time frame of the measurement. This ESA band contains a fast decay component ($\tau_1 = 0.41$ ps) and two slower contributions ($\tau_2 = 5.1$ ps and $\tau_3 = 82$ ps), which end up in a constant offset indicative for product absorption. Moreover, we investigated the *E* → *Z* isomerization for both molecules after $S_1(n\pi^*)$ excitation at $\lambda = 530$ nm.

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Following the Ultrafast Dynamics of a Bistable Intramolecular H-Transfer Switch by Time-Resolved Vibrational Spectroscopy

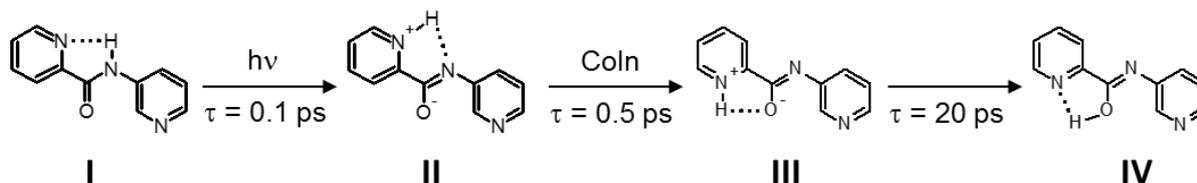
Hendrik Böhnke¹, Julia Bahrenburg¹, Michal F. Rode²,

Andrzej L. Sobolewski² and Friedrich Temps¹

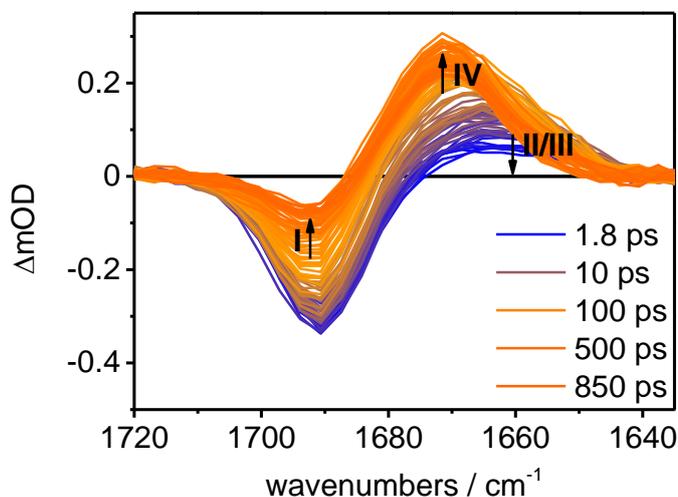
¹ *Institute of Physical Chemistry, Christian-Albrechts-University Kiel*

² *Institute of Physics, Polish Academy of Sciences*

Bistable intramolecular H-transfer systems are of substantial interest for photochromic molecular switches as the electronic deactivation happens on an ultrafast timescale and thus impedes undesired side reactions. Bistability may be realized by a structural rearrangement between reactant and photoproduct species. Here, we report on the photo-induced stepwise switching process of the bistable H-transfer switch N-(3-pyridinyl)-2-pyridine-carboxamide (NPPCA) by combined time-resolved spectroscopic techniques proposed by ab initio calculations.



Time-resolved fluorescence and electronic absorption spectroscopy yielded lifetimes of $\tau = 0.1$ ps and $\tau = 0.5$ ps associated with electronic deactivation via transient structures **I** and **II**. Monitoring the evolution of the wave packet back in the electronic ground state, transient electronic and vibrational absorption results indicate the formation of the final structure **IV** upon decay of intermediate structures **II** and/or **III** with $\tau = 20$ ps. Unambiguous evidence for the formation of form **IV** is provided by the rise of its prominent $\text{C}=\text{N}_{\text{stretch}}$ band at 1670 cm^{-1} . Likewise, the experimental transient vibrational spectra match the calculated ones of **I** and **IV** (MP2/aug-cc-pVDZ) well throughout the entire detection range recorded.



Photocontrol over molecular shape: synthesis and photochemical investigation of glycoazobenzene macrocycles

G. Despras^{1*}, J. Hain¹, S. O. Jaeschke¹

¹Christiana Albertina University of Kiel, Otto Diels Institute of Organic Chemistry, Otto-Hahn-Platz 4, 24098 Kiel, Germany

Unnatural macrocycles offer great opportunities for the design of functional molecules since the unique physicochemical properties they display can be finely tuned by the mean of organic synthesis.^[1] Carbohydrates are attractive building blocks for the preparation of macrocycles because they present several functional groups with a defined stereochemistry and also exhibit restricted conformational flexibility. Hence, numerous artificial macrocycles embedding sugar units have been synthesized and used in various applications, including supramolecular chemistry, catalysis or multivalency studies.^[2]

We envisioned the conception of glycomacrocycles able to switch between two defined structural forms upon light irradiation, in order to control their molecular features (e.g. physicochemical properties, chirality, cavity shape, spatial arrangement of side functional groups). Here, shape switching is based on the reversible *trans/cis* photoisomerization of an azobenzene hinge incorporated into the macrocycle backbone.^[3]

Cyclizing glucose- or maltose-based symmetrical azobenzene bis-glycosides with piperazine, through thiourea bridges, provided macrocycles (Fig. 1a) that display favorable photoswitching properties. The expected large amplitude shape modification and conformational stability were confirmed by NMR studies and molecular modeling. Importantly, our macrocycles also exhibit intriguing chiroptical behavior upon photoisomerization (Fig. 1a,b). In particular, circular dichroism measurements revealed that the *cis* isomers exist in a single *P* or *M* helical conformation, thus suggesting the *trans*→*cis* isomerization proceeds following an unidirectional motion.^[4]

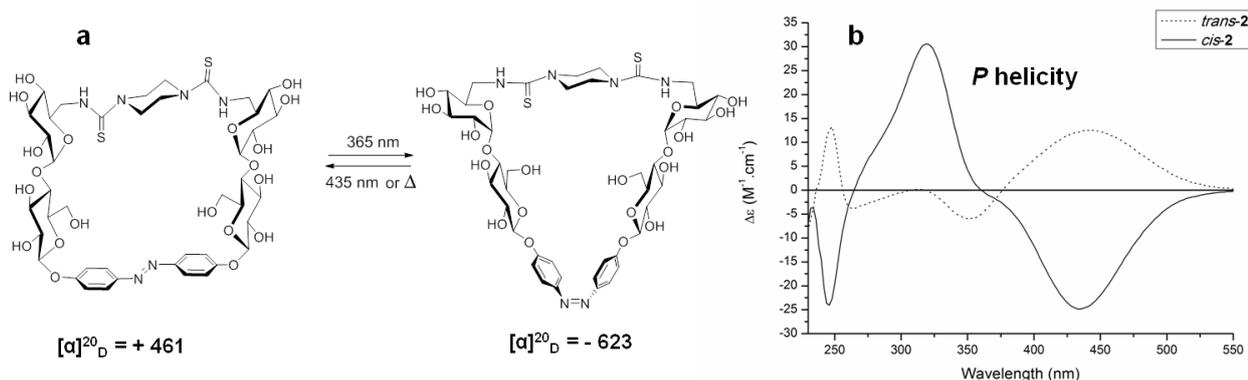


Figure 1. (a) Structure of the photoresponsive azobenzene maltoside macrocycle and the respective values of the specific rotation (c 0.05 in water) in the *trans* or *cis* state; (b) Circular dichroism spectra of the azobenzene maltoside macrocycle before (dotted line) and after irradiation (solid line) at 365 nm.

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Photoswitching of Azobenzene Glycoside Monolayers: Synthesis and Testing

E. Fast, V. Poonthiyil, A. Schlimm, F. Tucek, Th. K. Lindhorst*

Christiana Albertina University of Kiel, Otto Diels Institute of Organic Chemistry, Otto-Hahn-Platz 4, Kiel, Germany.

Glycocalyx, the carbohydrate-rich layer lining the outermost part of the endothelium, is one of the most important and intriguing surfaces in biology. Molecular interactions between glycocalyx components 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 also 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 However, literature reports suggest that dilution is not necessarily crucial for azobenzene isomerization on surfaces but it can also be achieved in SAMs with molecules possessing rigid backbones.^{3,4} Hence, here we report the synthesis of rigid bi- and terphenyl-derived azobenzene glycosides, and the characterization and photoswitchability of the resulting glyco-SAMs via IRRAS (infrared reflection adsorption spectroscopy). Also, in order to explore the effect of carbohydrate orientation in bacterial adhesion in a relatively complex glyco-SAMs, we will prepare mixed SAMs with two different types of azobenzene glycosides. The two ligands will be chosen in such a way that they undergo photoisomerization under different wavelengths and adhere to *E.coli* strains with different carbohydrate specificity. These orthogonal glyco-SAMs will be a better mimic of glycocalyx and will take us a step closer towards understanding the functioning of glycocalyx.

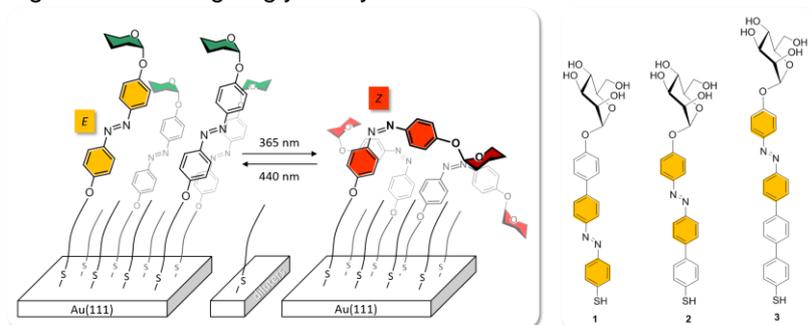


Figure 1. Photoswitchable azobenzene glycosides. Left: *E/Z* Photoisomerization of diluted glyco-SAMs; Right: Structures of the synthetic targets (azobenzene glycosides with rigid backbones) **1**, **2** and **3**.

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

Kim Fischer, Hannah Brandenburg

Prof. Dr. Felix Tuczek, 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 nickel(II) and 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 the first non-porphyrin based Ni(II) systems which show coordination-induced spin-state switching (CISSS). Ni(II) salpn complexes were investigated via Evans-NMR, UV/vis and ¹⁹F-NMR titration experiments. By determination of association constants and thermodynamic parameters for the coordination of axial ligands to unfunctionalized Ni(II) complexes a prediction of the switching behaviour of analogous LD-CISSS systems is possible.^[3] Furthermore, we generate tridentate iron(II) complexes as CISSS systems for analogous studies of the change in coordination number and a corresponding spin state switch.

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Novel Iron and Nickel complexes for spin state switching on surfaces and in solution

Jan Grunwald
CAU Kiel, Germany

Transition metal complexes have a broad variety in their physical and chemical properties. Spin crossover or spin state switching result in a change of some of those properties. Bistable systems with reversible switching between two spin states allow usage in several potential applications. Here we describe novel iron complexes that can be deposited on various surfaces, retaining their ability of thermal spin crossover and LIESST effect, with potential application in electronic storage devices. Furthermore, we describe ligand design and synthesis for novel nickel complexes. Irradiating a solution of which supposedly results in spin state switching (LD-CISS) with potential application as MRI contrast agents.

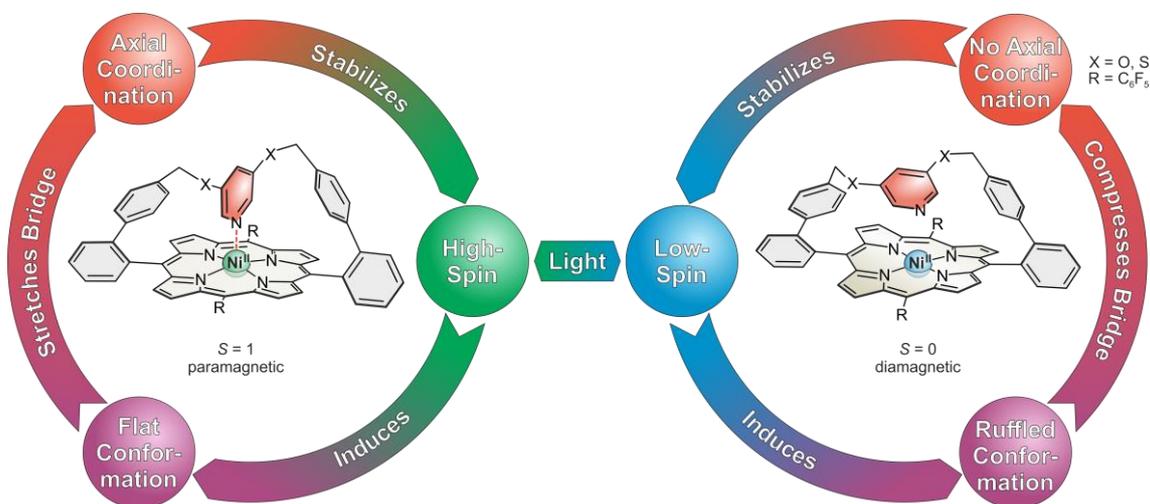
Photoswitching of Magnetic Bistable Strapped Nickel Porphyrins

Florian Gutzeit,¹ and Rainer Herges¹

¹ Otto Diels Institute for Organic Chemistry, Christian-Albrechts-University, D-24098 Kiel, Germany

Fax: +49-431-880-1558, Tel: +49-431-880-1929; E-mail: fgutzeit@oc.uni-kiel.de

Hair clip porphyrins combine the structural change and the ligand binding affinity of photoexcited nickel porphyrins into an intramolecular feedback.^[1-3] This feedback should allow a new highly efficient photoswitching mechanism of molecular magnetic properties without utilizing photochromic groups. The rigid bridge between two *meso*-substituents prevents the intramolecular coordination of the linked ligand in the ruffled conformation of the low spin state. After photoexcitation the bridge is stretched by the flattening of the porphyrin and forces the incorporated ligand close to the nickel ion. Subsequently axial coordination occurs due to increased ligand affinity of the nickel ion in the high spin state and stabilizes the paramagnetic isomer. By excitation of the paramagnetic isomer the process should be reversible. Compared to azopyridines the intended switching mechanism requires minimal movement and does not rely on photochemical reactions like conventional photochromic switches.^[4] Therefore switching should be feasible in solution as well as in solid state. Surface deposition is an established technique for porphyrins which extends the scope of the hair clip porphyrins. The transferability of the system between different environments opens up a variety of possible solution, surface and solid state analytics and applications.



Scheme 1. Scheme of the intramolecular feedback in Hair Clip Porphyrins towards photoswitching.

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Developing New LD-LISC Systems with Azo-functionalized Ligands as Photoswitches

Tammy Jacobsen-Bialas¹, H.-Leonie Fitschen, Sven Olaf Schmidt¹, Felix Tuczek¹

¹*University of Kiel, Max-Eyth-Straße 2, 24118 Kiel, Germany*

Tel: +49(0)4318805817, E-Mail: tjacobsen-bialas@ac.uni-kiel.de

Transition metal complexes that can undergo a thermal induced change of spin state between high spin and low spin are called spin crossover (SCO) complexes. This spin change can also be triggered by irradiation with light without altering the temperature. At very low temperatures this is called LIESST.^[1] For spin switching near room temperature a suitable photoisomerizable ligand is needed. The isomerization of the ligand induces a change in the ligand field strength and enables a spin transition. This effect is called ligand- driven light- induced spin change (LD- LISC) and allows for spin state switching on a molecular level.^[2]

In search for efficient LD-LISC complexes we employed 4- and 5-(phenylazo)-2,2'-bipyridine as a photoisomerizable ligand and investigated the SCO properties of the resulting Fe(II) complexes in the solid state and in solution. The results are compared to the literature-known parent complexes [Fe(bpz)₂(bipy)] and [Fe(NCS)₂(bipy)₂]. The complexes were also tested for LD-LISC behavior.^[3]

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Mounted switches on surfaces

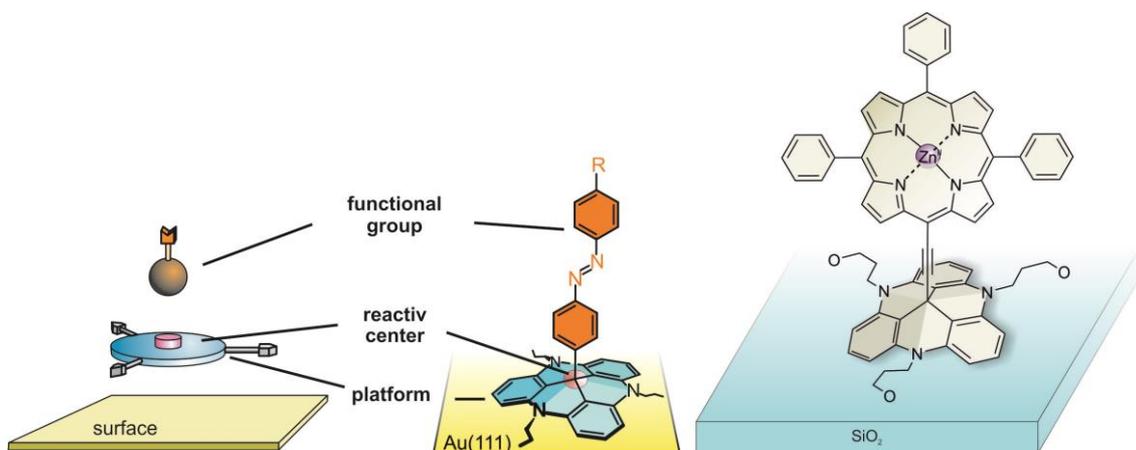
Torben Jäkel¹, Nicolai Krekieh², Olaf M. Magnussen² and Rainer Herges¹

¹*Institute for Organic Chemistry, Christian-Albrechts-University, Kiel, 24118 Germany*

Fax: +49-431-8801558, Tel: +49-431-8801929; E-mail: tjaekel@oc.uni-kiel.de

²*Institute for 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 porphyrins on quartz surfaces and detect their fluorescence. With the incorporation of a photoswitchable unit we want to observe fluorescence quenching on the quartz surfaces.



Reference

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Light-induced spin-state switching in Fe(II) spin-crossover thin films on TiTe₂ studied with NEXAFS

Simon Jarausch¹, Sebastian Rohlf¹, Matthias Kalläne¹, Benedikt Flöser², Felix Tuzcek², and Kai Rossnagel¹

¹Institut für Experimentelle und Angewandte Physik, CAU Kiel

¹Institut für Anorganische Chemie, CAU Kiel

E-mail: jarausch@physik.uni-kiel.de

Fe(II) coordination complexes are model systems for organic molecules whose electronic, magnetic, and structural properties can be manipulated by external stimuli. The temperature- and light-driven spin transitions observed in a number of these materials may provide a suitable testbed for the development of future spintronic devices. While the temperature- and light-induced spin-state switching of the spin-crossover (SCO) complex Fe(H₂B(pz)₂)₂(phen) adsorbed on Au(111) is well established^[1], this functionality is not preserved for molecules in direct contact to the surface due to molecular dissociation. To avoid this effect, one can either increase the stability of the SCO complex or reduce the substrate-mediated interactions. For the latter approach, the layered transition-metal dichalcogenide TiTe₂ may be a promising candidate due to its weak van der Waals-like interaction with adsorbates. Here, we present a near edge X-ray absorption fine structure (NEXAFS) spectroscopy study of the thermally and optically induced spin-state switching of Fe(PyPyr(CF₃)₂)₂(phen), a stabilized derivative of the aforementioned SCO complex, adsorbed on TiTe₂.

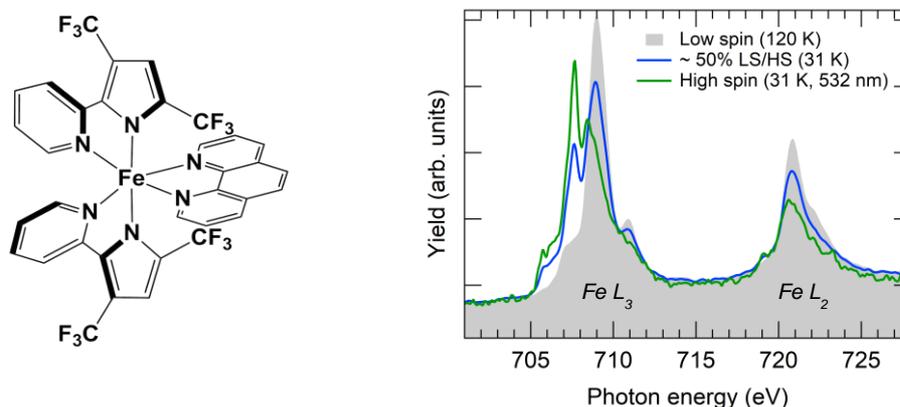


Figure 1: Left: Structure of the Fe(PyPyr(CF₃)₂)₂(phen) complex. Right: NEXAFS spectra of a Fe(PyPyr(CF₃)₂)₂(phen) thin film adsorbed on TiTe₂, measured at the iron L_{3/2} edge. Different spin states can be identified: The low spin state, measured at 120 K (grey filled curve), the high spin state, measured at 31 K under laser radiation of 532 nm (green line), and a mixed state, measured at 31 K (blue line).

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Conductance of a freestanding conjugated wire

T. Jasper-Tönnies*, A. Garcia-Lekue^{†‡}, T. Frederiksen^{†‡}, S. Ulrich[‡], R. Herges[‡], and R. Berndt*

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

[†]*Donostia International Physics Center (DIPC), Paseo Manuel de Lardizabal 4, Donostia-San Sebastián, Spain*

[‡]*IKERBASQUE, Basque Foundation for Science, Bilbao, Spain*

[‡]*Otto-Diels-Institut für Organische Chemie, Christian-Albrechts-Universität, 24098 Kiel, Germany*

A free-standing molecular wire is placed vertically on Au(111) using a platform molecule and contacted by a scanning tunneling microscope. Despite the simplicity of the single-molecule junction its conductance G reproducibly varies in a complex manner with the electrode separation. Transport calculations show that G is controlled by a deformation of the molecule, a symmetry mismatch between the tip and molecule orbitals, and the breaking of a $C\equiv C$ triple in favor of a Au-C-C bond. This tip-controlled reversible bond formation/rupture alters the electronic spectrum of the junction and the states accessible for transport, resulting in an order of magnitude variation of the conductance. Moreover, our results hint that it may be possible to design a mechanically controlled single molecule catalyst.

* Email address of presenting author:

something@mail.com



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Mahan Cone Formation in the Adsorbate System Tin-Phthalocyanine on Ag(111)

Stephan Jauernik¹, Petra Hein¹, Julian Falke¹, Max Gurgel¹ and Michael Bauer¹

¹Institute of Experimental and Applied Physics, University of Kiel, Germany

e-mail: jauernik@physik.uni-kiel.de

The adsorption of tin-phthalocyanine (SnPc) on Ag(111) has attracted considerable interest due to peculiarities in the adsorbate-substrate interaction and switching capabilities reported for this model-type organic/inorganic system [1,2]. In this work Low Energy Electron Diffraction (LEED) and Photoemission/Two-Photon Photoemission (PES/2PPE) are used to study how structural and electronic properties of this model system are correlated in the sub-monolayer coverage regime. Laser-based Photoemission data are recorded using a widely tuneable laser system offering the possibility to address various resonant transitions of the electronic structure at the metal/ organic interface. The study focusses on the temperature dependent structural phase transition between an incommensurate and commensurate adsorption phase which is accessible in the coverage regime between 0.90 ML and 0.94 ML. Notably, the incommensurate phase consists of a mixture of tin – up and tin – down orientated molecules whereas in the commensurate phase the tin – down configuration is predominant. PES data of SnPc/Ag(111) (Fig. 1(a) and Fig. 1(b)) reveal the formation of Mahan Cones [3] associated with direct optical transitions within the Ag sp-band [4] which are strongly modified in the presence of the adsorbate layer. Mahan cone simulations under consideration of the lattice structure of the SnPc overlayer along different high symmetry directions show a very good agreement with the experimental data (Fig. 1(c)).

Furthermore, 2PPE spectra reveal a binding energetic shift of the (n=1) image potential state (IPS) at the metal/organic interface at the transition from incommensurate to commensurate phase. This observation may be associated with a decrease of the effective adsorbate layer thickness as tin-up atoms are ‘switched’ into the tin-down position.

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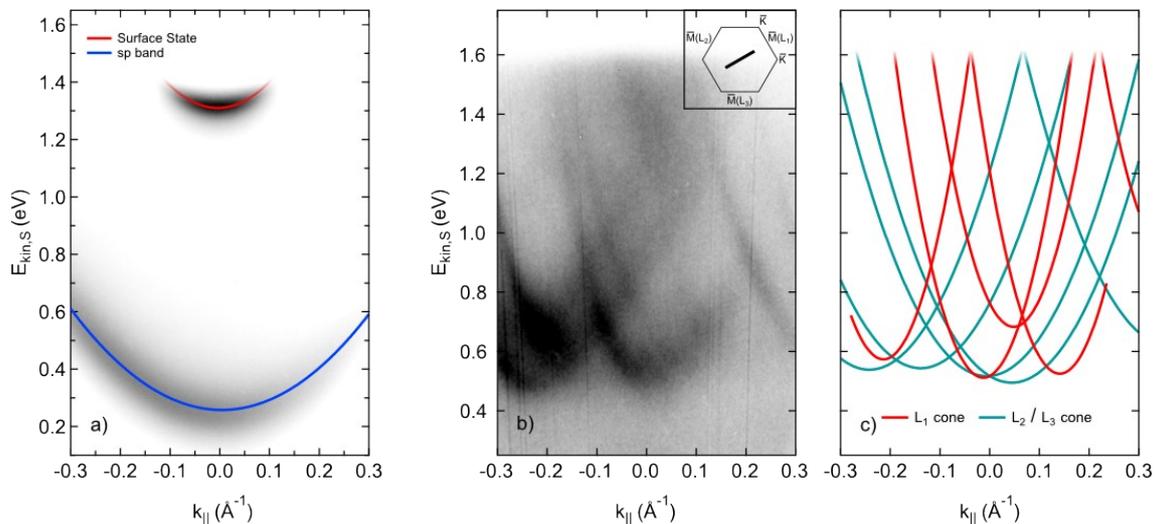


Fig. 1 PES intensity maps of (a) pristine Ag(111) and (b) 1ML SnPc/Ag(111) measured along the high symmetry direction GM; (c) Calculated Mahan cone cuts for 1 ML SnPc/Ag(111) under consideration of the lattice structure of the incommensurate SnPc overlayer

UV/Vis spectroscopy studies of molecular platforms on Au and SiO₂ Surfaces

Nicolai Krekiehnl¹, Robert Worm¹, Torben Jäkel², Sandra Ulrich², Rainer Herges², Olaf Magnussen¹.

¹Institut für Experimentelle und Angewandte Physik, Christian-Albrechts-Universität zu Kiel, 24098 Kiel, Germany

²Otto-Diels-Institut, Christian-Albrechts-Universität zu Kiel, 24098 Kiel, Germany

In the past we introduced the platform approach for the formation of self-assembled monolayers (SAMs) based on triazatriangulenium (TATA) platforms, whose structural properties (orientation of the function, lateral and vertical distances of the platforms) can be precisely controlled. The planar TATA molecule have three side chains, which are attached horizontally at the nitrogen atoms and control the intermolecular spacing. At the central carbon atom a functional photoactive group can be attached vertically via a spacer molecule (ethynyl group).

Here we present studies of these SAMs by UV/Vis spectroscopy, which is sensitive to the different absorption bands of the TATA platform as well as the photoactive group (azobenzene) [1]. This method provides insight on the TATA adsorption and the photoswitching of the molecules. Furthermore, by considering the directional dependence of the adsorbance on the orientation of the transition dipole moments relative to the electric field of the spectrometer beam, information about the adsorption geometry of the molecules can be obtained. UV/Vis spectra were measured in 1) simple normal-incidence transmission geometry, 2) attenuated total reflection geometry, and 3) combined variable incidence angle transmission and reflection measurements. In the last two cases experiments were performed in both s and p polarization, corresponding to an exclusively in-plane and a partial out-of-plane orientation of the electric field vector relative to the surface, respectively.

By these studies we were able to demonstrate the photoisomerization of azobenzene functionalized TATA molecules on Au and estimate the surface concentration [1]. In addition, it could be shown that TATA physisorbs on quartz substrates. Using TATA platforms with alcohol side chains, also chemisorbed adlayers can be prepared on quartz, which exhibit a perfectly planar orientation. Consequently, the platform concept is also applicable for this material. Similar UV/Vis studies on 200 nm thick Au(111) films on Si wafers likewise confirmed a planar orientation of the molecules on the surface.

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Synthesis And Characterization Of Photoswitchable Receptors For Oxoanion Condensation

F. Kruse¹, Prof. Dr. R. Herges¹
¹*Otto-Diels-Institut für Organische Chemie,
Otto-Hahn-Platz 4, 24118 Kiel*

E-mail: 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. 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.

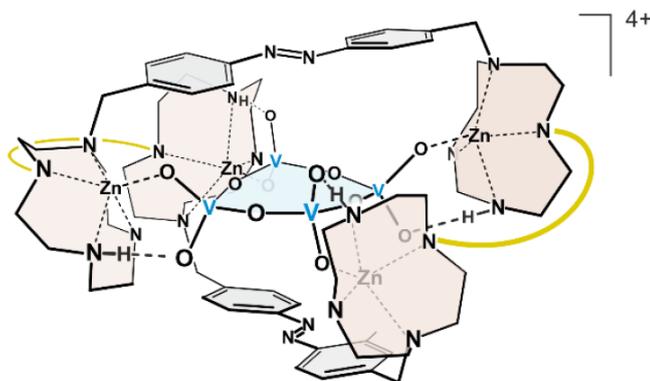


Figure 1: Covalent linkage of two receptor molecules for the complexation of tetravanadate.

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A Molecular Assembler for Phosphate Condensation

Lisa Leben¹, Christian Schütt¹, Benedikt M. Flöser², Felix Tuczec² and Rainer Herges¹

¹Institute for Organic Chemistry, Christian-Albrechts-University, Kiel, 24118 Germany

Fax: +49-431-8801558, Tel: +49-431-8801926; E-mail:

lleben@oc.uni-kiel.de

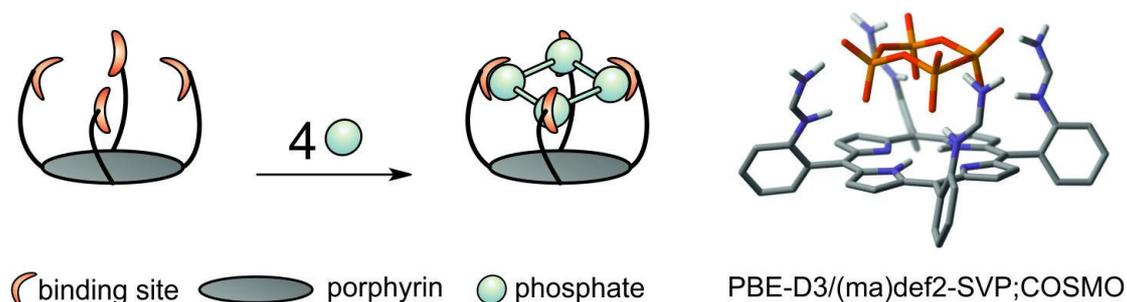
²Institute for Inorganic Chemistry, Christian-Albrechts-University, Kiel, 24118 Germany

ATP-synthase is an enzyme that is able to condensate adenosine diphosphate and monophosphate to adenosine triphosphate which is a natural energy storage.¹ This work is focused on building an artificial assembler that is able to condensate monophosphate to oligophosphate in order to mimic ATP-synthase.

Based on quantum chemical calculations this receptor is designed to strongly bind cyclo tetraphosphate. Due to the higher affinity of the tetramer compared to the monomer the condensation reaction inside the receptor is highly favored.

The assembler consists of a *meso*-substituted porphyrin as a scaffold and amidinium or guanidinium units as binding sites. This design fits in size and four-folded symmetry to the tetramer which after release hydrolyses to the stable linear triphosphate to overcome microscopic reversibility.

In previous works we were already able to proof this kind of receptor assisted condensation for vanadate.² This is a new approach to enable the more energy consuming condensation of phosphate.



Scheme 1. Sketch and calculated structure of the receptor for phosphate condensation.

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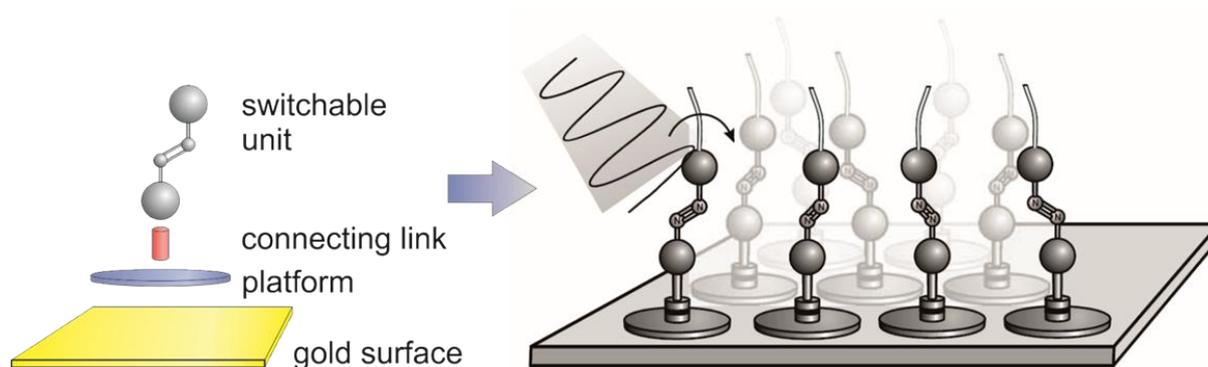
Azo Functionalized TATA Platforms

Roland Löw¹, Rainer Herges¹

¹*Otto Diels-Institute of Organic Chemistry, Christian-Albrechts-University,
Otto-Hahn-Platz 4, 24118 Kiel, Germany*

Tel: +49 +431 880-3229; E-mail: rloew@oc.uni-kiel.de

The azo TATA (triazatriangulenium) platform concept can be used for the functionalization of surfaces and is supposed to reach an oriented transport of particles or molecules. For a sterically unhindered light-induced switching process between *trans* and *cis* isomers the azobenzene units need a certain distance to each other. For this requirement the azobenzenes are functionalized over a spacer on triazatrianguleniumions, which serves as platforms. Certainly the azobenzenes have different thermal relaxation times in solution and on gold surfaces from the *cis* back to the *trans* configuration. While the relaxation times in solution are in the range of hours, on gold surfaces the back relaxation happens in the seconds scale. With different spacer units it is possible to enhance the thermal relaxation times of the azo unit especially on gold surfaces.^[1]



Scheme 1. Shown is a modular system of the azo TATA platform concept. The size of the platform determines the distance between the functional molecules on gold surfaces and the linker connect the switchable unit with the platform. The azo unit can be switched with different wavelength between the *cis* and *trans* isomer.^[2]

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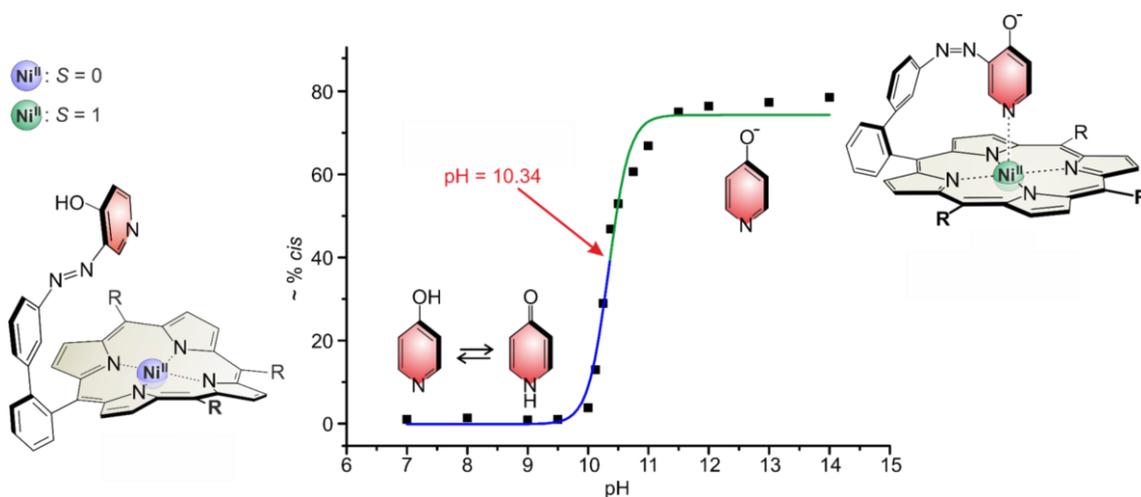
Temperature- and pH-responsive Photo Switchable Contrast Agents for Nuclear Magnetic Resonance Imaging (MRI)

Jannis Ludwig, Marcel Dommaschk, Jens Gröbner and Rainer Herges

Institute for Organic Chemistry, Christiana-Albertina-University, Kiel, 24118 Germany

Fax: +49-431-880-1558, Tel: +49-431-880-1927; E-mail: jludwig@oc.uni-kiel.de

The increasing importance of magnetic resonance imaging (MRI) as a non-invasive medical diagnostic tool leads to new requirements towards MRI contrast agents to improve imaging quality and enable new imaging options. Common gadolinium based contrast agents improve the contrast, related to their magnetic properties and local concentration.^[1] Recently developed functional contrast agents are able to respond dynamically to specific parameters (e.g. temperature, pH-value). Overcoming the concentration-dependence is the main challenge for responsive contrast agents.^[2] HERGES *et al.* reported on Ni(II)-porphyrins switching their coordination geometry and thus their spin state by light-driven control of the ligands' coordination. The underlying principle was coined Light-Driven Coordination-Induced Spin State Switch (LD-CISSS) and allows to switch between a paramagnetic, MRI-active and diamagnetic, MRI-silent complex.^[3] Previously developed systems with azopyridines as covalently bonded photo switchable ligand ("recordplayer concept") show a light-driven spin state switch in organic solvents but are unsuitable for MRI measurements in water. This work is focused on the improvement of the "recordplayer concept" for the concentration independent application as MRI contrast agent in aqueous solution. Therefore, stronger axial ligands at the switching unit are required. Furthermore new switches with pH-responsive functional groups are investigated and MRI measurements have been performed.



Scheme 1. The pH-dependent switching behavior of the hydroxyl-recordplayer molecule is shown.

Reference

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Physical Vapour Deposition of Fe(II) SCO Complexes

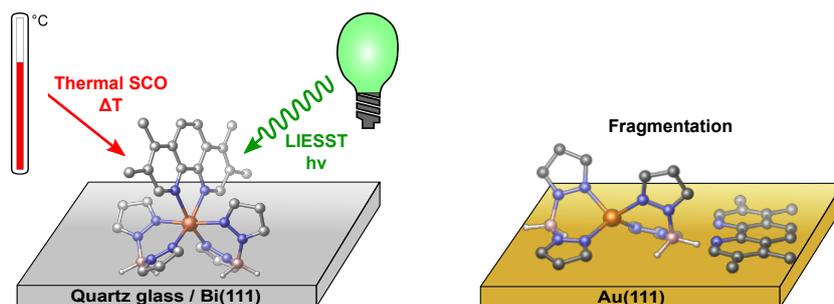
Sascha Ossinger*, Holger Naggert*, Lalminthang Kipgen⁺, Torben-Jasper Tönnies[§],
Wolfgang Kuch⁺, Richard Berndt[§] and Felix Tuczek*

*University of Kiel, Institute for Inorganic Chemistry
Max-Eyth-Str. 2, 24118 Kiel, Germany
E-mail: sossinger@ac.uni-kiel.de

⁺University of Berlin, Institute for Experimental Physics

[§]University of Kiel, Institute for Experimental and Applied Physics

Spin crossover (SCO) transition-metal complexes 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 spintronics.¹ Transitions between diamagnetic low-spin (LS, S=0) and paramagnetic high-spin (HS, S=2) states of these complexes can be induced by stimuli like temperature (thermally SCO) and light (LIESST/reverse-LIESST).² We synthesized a few octahedral iron(II) spin crossover (SCO) complexes with the general formula $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2\text{L}]$ with pz = pyrazole and L = coligand (like 2,2-bipyridine and 1,10-phenanthroline). They have been successfully vacuum deposited and characterized on various surfaces (quartz, Au(111), Bi(111) and HOPG) compared to the bulk material.^{3,4,5}



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⁵S. Ossinger, H. Naggert, L. Kipgen, T. Jasper-Toennies, A. Rai, J. Rudnik, F. Nickel, L. M. Arruda, M. Bernien, W. Kuch, et al., *J. Phys. Chem. C* **2017**, 121, 1210-1219.

Multi-functional polymer micro- and nano-fibers fabricated by centrifugal spinning

Ruchira Pereira^{1,2}, Sindu Shree¹, Leonard Siebert¹, Mathias Schulz², Rainer Adelung¹, Anne Staubitz^{2,3}

¹*Institute for Materials Science, Functional Nanomaterials, University of Kiel, Kaiserstr. 2, 24143 Kiel, Germany*

²*Otto-Diels-Institute for Organic Chemistry, University of Kiel, Otto-Hahn-Platz 4, 24118 Kiel, Germany*

³*Institute for Organic and Analytical Chemistry, University of Bremen, Leobener Str. NW2 C, 28359 Bremen, Germany*

Nano- and micro-fibers have a plethora of applications in the fields of tissue engineering, filtration membranes, functional textiles, electrodes for supercapacitors, energy storage devices, etc. The commercialisation of the widely used technique of electrospinning, to produce nano-fibers is restricted due to its low production rate. Centrifugal spinning offers the possibility to fabricate fibers from a variety of polymer solutions at high speed and low cost. Synthetic chemistry enables us to design pathways, to covalently incorporate spiropyran moiety into the backbone of different polymers, opening several doors to construct dynamic materials. These functionalised polymers were processed using centrifugal spinning, by injecting the solution into the rotating spin head. Only when a critical rotation speed is achieved, the centrifugal force overcomes the surface tension, ejecting the liquid jet out from the nozzle and depositing the solidified fibers at the collector. The focus of this work is, to study the effect of - the concentration (of polymer solutions in wt. %), nozzle diameter, rotational speed on the diameter, morphology of the obtained fibers and its possible applications as functional materials.

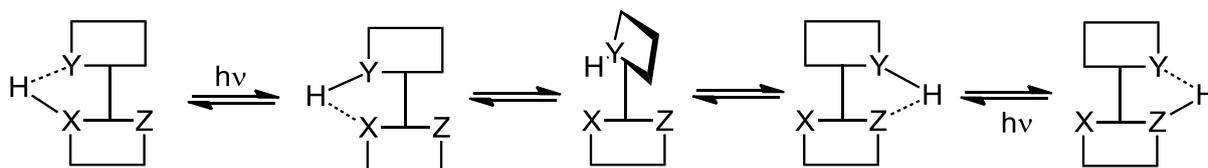
Synthesis of ESIPT Switch Capable Quinolines

Jesper Rönn, Ulrich Lüning

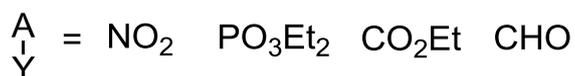
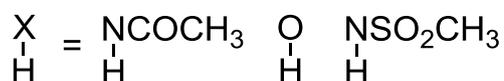
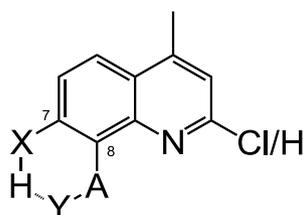
Otto-Diels Institut für Organische Chemie, Otto-Hahn Platz 4, 24118 Kiel

Email: jroenn@oc.uni-kiel.de

Objective of this project is the development of ESIPT switch capable molecules. Excited-state intramolecular proton transfer (ESIPT) is of huge interest because of its fast chemical reactions (20-100 fs) and its high application potential. ESIPT switch capable molecules should be bistable and convertible from one form to the other selectively by light at different wavelengths.



In order to obtain ESIPT switch capable molecules, substituted quinolines were synthesized containing intramolecular hydrogen bonds. Different hydrogen donors were introduced at position 7 and different hydrogen acceptors at position 8.



STM studies of functional platform adlayers on Au(111) surfaces

Talina R. Rusch¹, Melanie Hammerich¹, Roland Löw², Alexander Schlimm³, Felix Tuczek³, Rainer Herges² and Olaf M. Magnussen¹

¹*Institute of Experimental and Applied Physics, Kiel University, Germany*

²*Otto Diels Institute of Organic Chemistry, Kiel University, Germany*

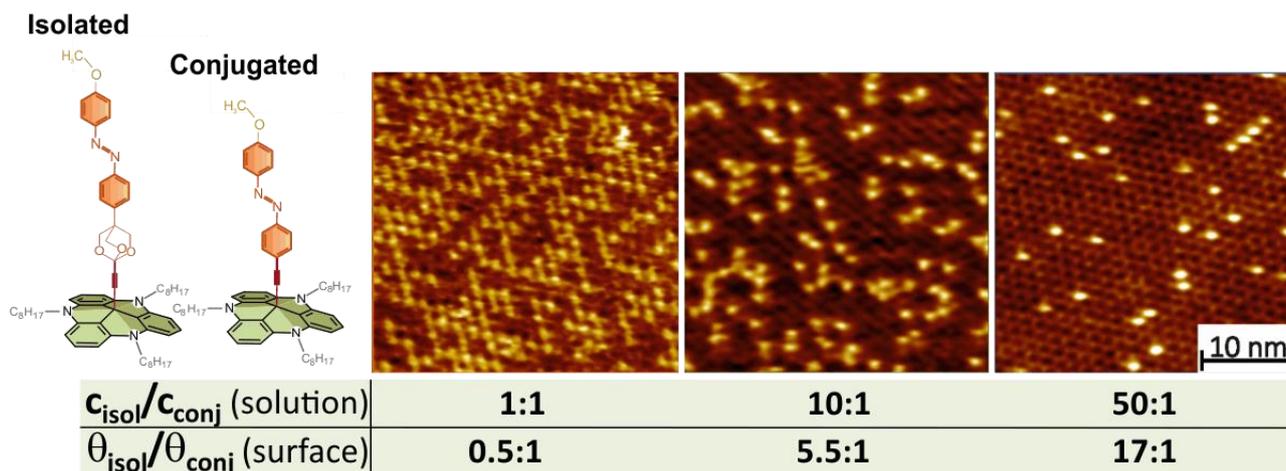
³*Institute of Inorganic Chemistry, Kiel University, Germany*

rusch@physik.uni-kiel.de

Abstract. The functionalization of surfaces by self-assembled monolayers is of great interest in nanoscience. We have introduced the so called platform approach, where molecular platforms of Triazatriangulenium (TATA) [1, 2, 3] ions are employed for attaching freestanding functional units to metal surfaces. These platforms provide a well-defined lateral and vertical molecular architecture. The steric demand is controlled by different alkyl side chains and the vertical functional group is attached covalently to the central carbon atom.

Here, detailed STM studies on different adsorbate layers of TATA derivatives are presented. Specifically, we will discuss the structure of adlayers consisting of two different TATA derivatives, one where the attached azobenzene is fully conjugated and one where it is isolated. Furthermore, we will present direct STM observations of the photoswitching in azobenzene functionalized TATA adsorbate layers.

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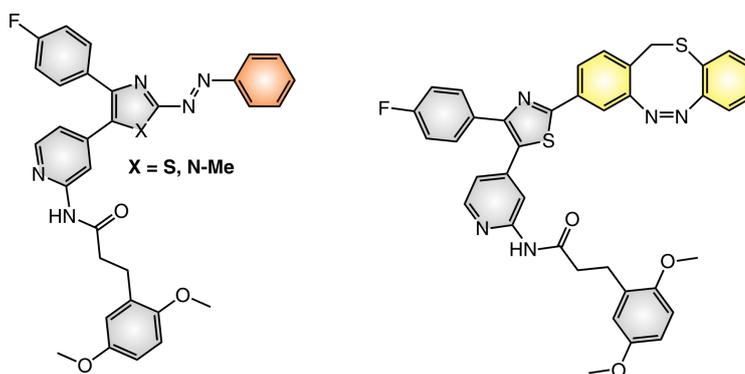
Photoswitchable Protein Kinase Inhibitors for Novel Anticancer Applications

Miriam Schehr,^a Rainer Herges,^a Christian Peifer,^b

^a Institute of Organic Chemistry, Christian-Albrechts-University of Kiel
(mschehr@oc.uni-kiel.de)

^b Institute of Pharmacy, Christian-Albrechts-University of Kiel

In the last couple of years kinase inhibitors have become one of the most employed group of drug targets.¹ Today there are more than thirty different kinase inhibitors on the market used mostly against a variety of different cancer types. But most kinase inhibitors exhibited poor selectivity between kinases.² Our goal is to design, synthesize and characterize a reversible photoswitchable kinase inhibitor, which can be spatial and temporal controlled by light to minimize the risk of side effects or resistances. In addition such a photoswitchable inhibitor could be of great interest to investigate the mechanism of inhibition on a molecular level. Therefore we use 4,5-diarylthiazol and -imidazole units as core structures which already have been proven as potential building blocks for kinase inhibitors.³ The 2-position of the heterocycles can be used for the functionalization with a photoswitchable unit like azobenzene or diazocine derivatives.



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Tuning the Relaxation Kinetics of Surface-Adsorbed Azobenzenes by Orders of Magnitudes: A IRRAS Study of Azobenzene-Functionalized Triazatriangulene Platforms on Au(111)

Alexander Schlimm¹, Hanne Jacob¹, Roland Löw², Talina Rusch³, Fynn Röhrich², Olaf Magnussen³, Rainer Herges², Felix Tüczek¹

¹University of Kiel, Max-Eyth-Straße 2, 24118 Kiel, Germany

²University of Kiel, Otto-Hahn-Platz 4, 24118 Kiel, Germany

³University of Kiel, Leibnizstraße 19, 24118 Kiel, Germany

Fax: +49(0)4318801520, Tel: +49(0)4318805816; E-mail: aschlimm@ac.uni-kiel.de

Monolayers of photoswitchable molecules on surfaces are of significant interest with respect to applications in data storage, sensors and molecular electronics.^[1] At present, the relaxation behavior of azo compounds on gold surfaces is not understood. For this reason we designed different azo-TATA compounds and investigated their switching and relaxation behavior on gold. Our method of choice for monitoring the thermal backrelaxation as well as determining the half-life of the various azobenzene-TATA systems is Infrared-Reflection-Absorption-Spectroscopy (IRRAS). The orientation of C_{phenyl}-O_{methoxy} stretch with regard to the surface changes by means of the *cis/trans* isomerization (Fig. 1).

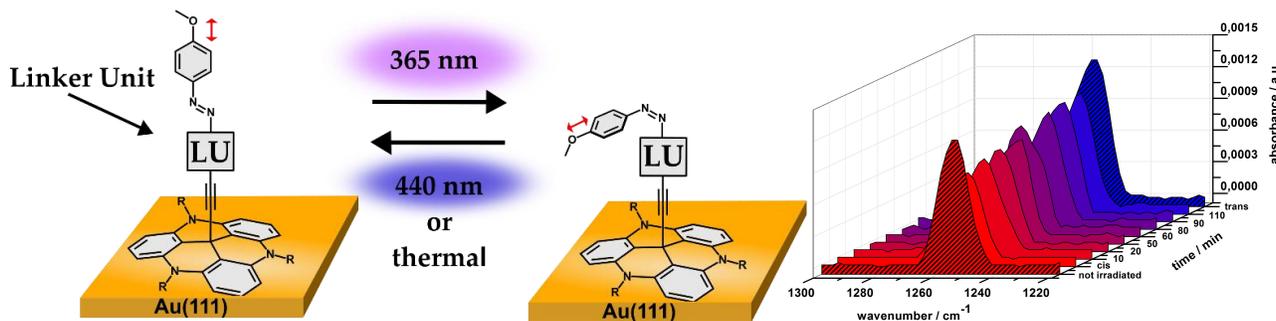


Figure 1: The platform approach: general scheme for azobenzene-TATA systems on Au(111) (left), thermal backrelaxation monitored by IRRAS (right).

Even though the azobenzene is not directly in contact with the gold surface, the half-life period is significantly different than in solution. While the relaxation times in solution are in the range of hours, on a gold surface the relaxation for some systems proceeds in seconds or minutes.^[2] We could show that the relaxation behavior of the azo-TATA on Au(111) surfaces largely depends on the linker unit between platform and azo moiety (Fig. 1).

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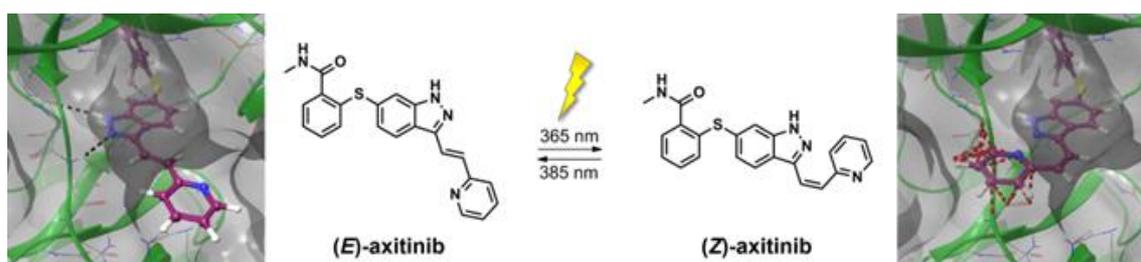
A Photoswitchable Kinase Inhibitor: Photoinduced *E/Z* Isomerization of Axitinib

Dorian Schmidt,¹ Linda Heintze,¹ Theo Rodat,¹ Rebecca Horbert,¹
Jantje Weber,¹ Christian Renn,¹ Boris Pinchuk,¹ Christian Peifer^{1,*}

¹Institute of Pharmaceutical Chemistry, University of Kiel, Kiel, 24118, Germany
E-mail: dschmidt@pharmazie.uni-kiel.de, cpeifer@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 drug targets and the development of small molecule kinase inhibitors has become a major field in pharmaceutical research. [1]

Our goal is to develop photoswitchable kinase inhibitors that can be spatially and temporally controlled by light. These compounds will be useful not only for innovative therapeutic approaches but also as novel pharmacological tools, e.g. for resolving dynamic aspects of kinase signal transduction.



Scheme 1. (Left): (*E*)-axitinib in the ATP binding pocket of VEGFR2 (pdb code 4AG8). [2]. (Right): Superposition with (*Z*)-axitinib (steric clashes with the protein are indicated as red dotted lines).

In the present study, we focused on the protein kinase inhibitor axitinib which is approved for advanced metastatic renal cell carcinoma (RCC) since 2012. Interestingly, axitinib undergoes an *E-Z* isomerization upon irradiation with UV light (Scheme 1). [3] Hence, our goal was to explore if its inhibitory effect can be turned “on” and “off” triggered by light.

Indeed, we could demonstrate that (*Z*)-axitinib is up to 43 times less active in an *in vitro* VEGFR kinase assays and 19 times less active on human umbilical vein endothelial cells (HUVEC) compared to (*E*)-axitinib. By irradiating (*Z*)-axitinib with UV light (385 nm) it is possible to switch it completely to the (*E*)-isomer and to restore the biological activity of (*E*)-axitinib. However, *vice versa* it is not possible to switch the biological activity of (*E*)-axitinib “off” in aqueous solution.

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Macrocyclic mechanophores for investigation by AFM

using the safety line concept

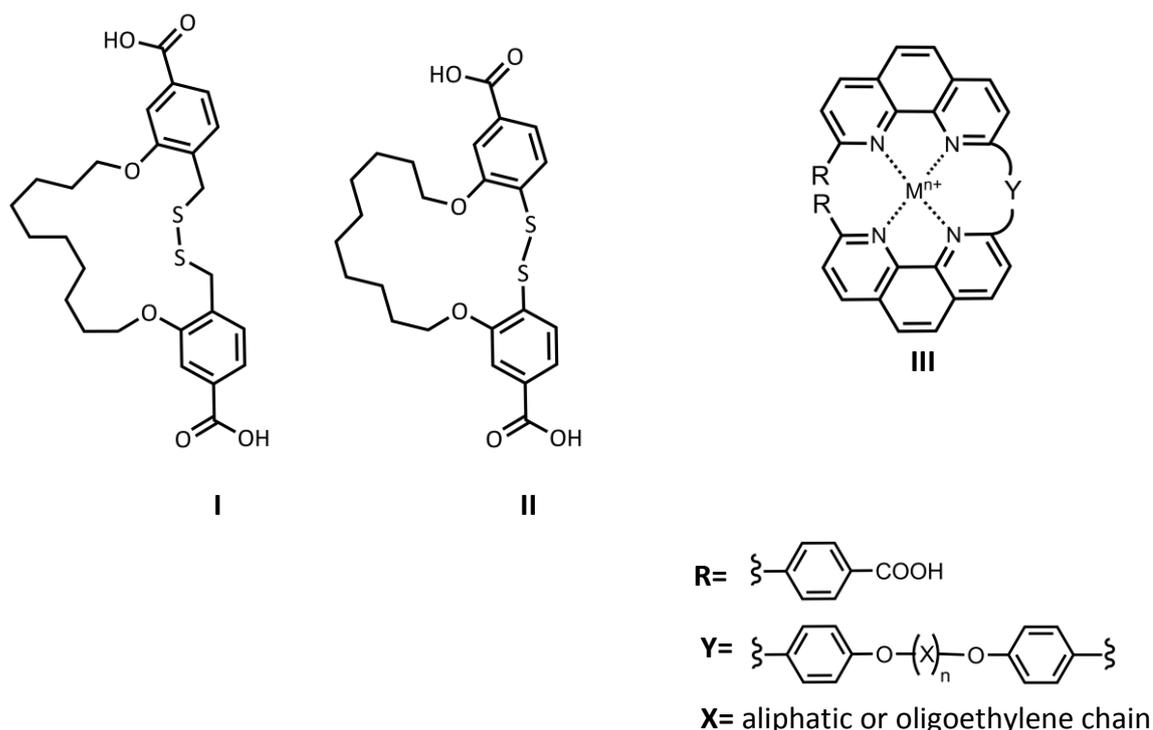
Nelli Schuller, Ulrich Lüning

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

Email: nschuller@oc.uni-kiel.de

A mechanophore is a force-sensitive molecular unit that offers mechanically labile bonds. By applying a mechanical force to mechanophores they will undergo chemical transformations. One example for chemical transformation is the cleavage of covalent or coordinative bonds. The required mechanical force to cleave these bonds can be measured and investigated by AFM (*atomic force microscopy*) single molecule spectroscopy. To pinpoint the mechanical induced bond rupture, the mechanophore is embedded into a macrocycle with a safety line.

Current work deals with the synthesis of macrocyclic disulfides **I** and **II** as well as macrocyclic complexes **III**. The reversibility of bond rupture shall be investigated by AFM to understand the mechanism of disulfide bond reactions in proteins, e.g. protein folding and unfolding.



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LD-CISSS within the Biooptical Window

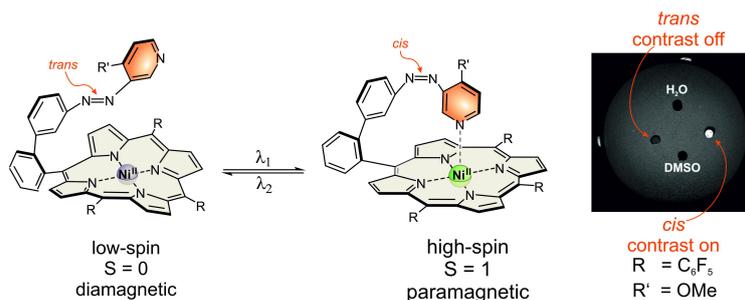
M.Sc. Vanessa Thoms,^a Dr. Marcel Dommaschk^b and Prof. Dr. Rainer Herges^c

^a Otto Diels-Institute of Organic Chemistry, Otto-Hahn-Platz 4, 24118 Kiel, Germany, email: vthoms@oc.uni-kiel.de

^b Otto Diels-Institute of Organic Chemistry, Otto-Hahn-Platz 4, 24118 Kiel, Germany

^c Otto Diels-Institute of Organic Chemistry, Otto-Hahn-Platz 4, 24118 Kiel, 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 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).^[1-3]



Scheme 1. Reversible light-induced magnetic switching of an azopyridine functionalized Ni(II)porphyrin ($R = C_6F_5$, $R' = H$, $\lambda_1 = 500$ nm, $\lambda_2 = 430$ nm) (left)^[1-3] and 3 T magnetic resonance image of 3 mM record player solutions in DMSO (right).^[4]

To achieve maximum efficiency in MRI contrast switching, the intramolecular coordination between the Ni(II)platform and the photoswitchable azopyridine has to be amplified resulting in an increased transformation to the paramagnetic *cis* species.^[5] One possibility to improve the intramolecular coordination is the use of chlorins and (iso)bacteriochlorins as new record player platforms. A second advantage of these porphyrinoids are the bathochromic shifted absorption bands. Hence, these molecules can be addressed within the biooptical window (near infrared, NIR) which is important for in vivo applications.^[6] The next step is to make these molecules watersoluble.

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

Jonas Warias
CAU Kiel, Germany

The mechanical and dynamic properties of phospholipid membranes are of importance for important biological functions, such as switching of embedded proteins. 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). This allows us to reversibly change the azobenzene-glycolipid orientation between trans- and cis-conformation by illumination with UV and blue light. We have followed the structural changes in this model membrane and the switching kinetics of the system with Langmuir isotherms and in situ X-ray reflectivity at the LISA diffractometer P08, PETRA III. Strong changes in membrane conformation upon switching have been observed, and a critical point has been discovered above which the membrane expands rather than compresses upon switching.

LIST OF PARTICIPANTS

- Prof. Dr. Rainer Adelung**, Kiel, Germany
Reihaneh Amirbeigi Arab, Kiel, Germany
Dennis Bank, Kiel, Germany
Prof. Dr. Michael Bauer, Kiel, Germany
Hendrik Böhnke, Kiel, Germany
Prof. Dr. Richard Berndt, Kiel, Germany
Prof. Dr. Stefan Bräse, Karlsruhe, Germany
Jasna Brekalo, Kiel, Germany
Dr. Guillaume Despras, Kiel, Germany
Dr. Marcel Dommaschk,
Manchester United Kingdom
Prof. Dr. Karl-Heinz Ernst, Dübendorf Switzerland
Ellen Fast, Kiel, Germany
Dr. Sven Festersen, Kiel, Germany
Kim Daniela Fischer, Kiel, Germany
H.-Leonie Fitschen, Kiel, Germany
Achim Fölster, Kiel, Germany
Leon Merten Friedrich, Kiel, Germany
Jan Simon v. Glasenapp, Kiel, Germany
Dr. Giovanni Granucci, Pisa, Italy
Malte Großmann, Kiel, Germany
Dr. Jens Groebner, Kiel, Germany
Dr. Manuel Gruber, Kiel, Germany
Jan Grunwald, Kiel, Germany
Florian Gutzeit, Kiel, Germany
Julia Hain, Kiel, Germany
Dr. Soumyajyoti Haldar, Kiel, Germany
Sebastian Hamer, Kiel, Germany
Prof. Dr. Bernd Hartke, Kiel, Germany
Prof. Dr. Stefan Heinze, Kiel, Germany
Prof. Dr. Rainer Herges, Kiel, Germany
Daniel Hugenbusch, Rodenbek, Germany
Malte Jacobsen, Kiel, Germany
Tammy Jacobsen-Bialas, Kiel, Germany
Sven Ole Jaeschke, Kiel, Germany
Simon Jaraus, Kiel, Germany
Torben Jasper-Tönnies, Plön, Germany
Stephan Jauernik, Kiel, Germany
Torben Jäkel, Kiel, Germany
Prof. Dr. Nathalie Katsonis, Enschede, Netherlands
Prof. Dr. Rafal Klajn, Rehovot, Israel
Birthe Kohly, Sörup, Germany
Bahne Krahwinkel, Kiel, Germany
Nicolai Krekielehn, Kiel, Germany
Fabian Kruse, Kiel, Germany
Daniel Langbehn, Kiel, Germany
Dr. Jérémie Léonard, Strasbourg France
Roland Löw, Kiel, Germany
Prof. Dr. Ulrich Lüning, Kiel, Germany
Lisa Leben, Kiel, Germany
Prof. Dr. David A. Leigh, Manchester, UK
Pascal Lentjes, Kiel, Germany
Shuo Li, Kiel Germany
Prof. Dr. Christoph Lienau, Oldenburg, Germany
Jannis Ludwig, Kiel, Germany
Prof. Dr. Olaf Magnussen, Kiel, Germany
Lisa Müller, Kiel, Germany
Prof. Dr. Anna McConnell, Kiel, Germany
Sebastian Megow, Kiel, Germany
Tobias Moje, Kiel, Germany
Dr. Bridget Murphy, Kiel, Germany
Tjorge Neumann, Kiel, Germany
Sascha Ossinger, Kiel, Germany
Tobias Paschelke, Kiel, Germany

Prof. Dr. Christian Peifer, Kiel, Germany

Morten Peters, Kiel, Germany

Ruchira Pereira, Kiel, Germany

Dr. Vivek Poonthiyil, Kiel, Germany

Dr. Marc Heinrich Prosenç,
Kaiserslautern, Germany

Fynn Röhricht, Kiel, Germany

Jesper Rönn, Kiel, Germany

Franziska Reise, Kiel, Germany

Prof. Dr. Vincent Repain, Paris, France

Sebastian Rohlf, Kiel, Germany

Prof. Dr. Kai Rossnagel, Kiel, Germany

Talina Rusch, Kiel, Germany

Andrea Sartori, Kiel, Germany

Dr. Achim Schöll, Würzburg, Germany

Miriam Schehr, Kiel, Germany

Alexander Schlimm, Kiel, Germany

Dorian Schmidt, Kiel, Germany

Nelli Schuller, Kiel, Germany

Mathias Schulz, Kiel, Germany

Sindu Shree, Kiel, Germany

Bill Brook Shurtleff, Kiel, Germany

Julia Siekmann, Kiel, Germany

Carina Spormann, Kiel, Germany

Insa Stamer, Kiel, Germany

Prof. Dr. Anne Staubitz, Bremen, Germany

Rebecca Stellmacher, Kiel, Germany

Dr. Thomas Strunskus, Kiel, Germany

Prof. Dr. Friedrich Temps, Kiel, Germany

Vanessa Thoms, Kiel, Germany

Prof. Dr. Felix Tuczek, Kiel, Germany

Wiebke Wagner, Kiel, Germany

Shuangqing Wang, Kiel, Germany

Jonas Warias, Kiel, Germany

Prof. Dr. Christof Wöll, Karlsruhe, Germany

Prof. Dr. Hermann A. Wegner, Giessen, Germany

Dr. Torsten Winkler, Kiel, Germany

Robert Worm, Kiel, Germany