

MO 21: Ultrafast Dynamics II

Time: Thursday 14:30–16:45

Location: HS 3044

MO 21.1 Thu 14:30 HS 3044

Reversible Switching based on intramolecular long-range Proton Transfer — CHRIS REHHAGEN¹, MIGUEL ARGÜELLO CORDERO¹, FADHIL KAMOUNAH², VERA DENEVA³, IVAN ANGELOV³, MARVIN KRUPP¹, SØREN SVENNINGSEN², MICHAEL PITTELKOW², STEFAN LOCHBRUNNER¹, and LIUDMIL ANTONOV³ — ¹Institute for Physics and Department of Life, Light and Matter, University of Rostock, 18059 Rostock, Germany — ²Department of Chemistry, University of Copenhagen, DK-2100 Copenhagen, Denmark — ³Institute of Electronics, Bulgarian Academy of Sciences

A molecular switch is one of the essential elements in molecular electronics. The main requirement in the design of molecular switches is to provide a fast and clean interconversion between structurally different molecular (on- and off-) states. Currently existing molecular switches are either chemically or light driven. The proton transfer could be a new and attractive elementary switching process, because the change in the tautomeric state is always accomplished by a fast proton exchange between the reaction centers in the same molecule. The energy required for proton transfer is fairly low, which provides the opportunity for fueling with visible and near infrared light. Therefore, absorption and emission spectra of a new compound HQBT are investigated and further characterized with femtosecond transient absorption spectroscopy. The system consists of a benzothiazole rotor attached to a 7-hydroxy quinoline stator. A clean and ultrafast off-/on- switching, based on intramolecular long-range proton transfer, is observed in solution.

MO 21.2 Thu 14:45 HS 3044

Unraveling the photochemistry of Ti^{IV}Cp₂(NCS)₂ — JONAS SCHMIDT, LUIS IGNACIO DOMENIANNI, MARCEL LEUCHNER, ANDREAS GANSÄUER, and PETER VÖHRINGER — Rheinische Friedrich-Wilhelms-Universität, Bonn, Deutschland

Recently, we reported the observation of the entry event of Ti^{IV}Cp₂(NCS)₂ into a photocatalytic cycle in real-time.^[1] In this study we were able to show the thermally activated delayed fluorescence of Ti^{IV}Cp₂(NCS)₂ after excitation with 450 nm light. Furthermore, we were able to observe the reductive quenching of the reactive triplet state with NPH₃ as an electron donor using time-resolved spectroscopy.

In a further step, we now want to investigate the following steps in the catalytic cycle. Therefore, we employ a substrate that acts as the amine electron donor to reduce the titanocene as well as the epoxide for radical arylation. To achieve this goal, we will utilize the long pump-probe delays of up to 300 μs of our synchronized double Ti:Sapphire regenerative amplifier setup for fs-UV/Vis-pump/mIR-probe spectroscopy. To aid the analysis of the spectroscopic findings, we will employ density functional theory as well as cooperate with synthetic chemists. From these experiments, we hope to gain further insight into the later mechanism of the photocatalytic cycle as it is still unclear if one or two equivalents of the substrate are involved.

Literature:

[1] J. Schmidt et al., *Angew. Chem. Int. Ed.* **2023**, *62*, e202307178.

MO 21.3 Thu 15:00 HS 3044

Ultrafast Formation of Metallo-Nitrenes — MARKUS BAUER, LUIS DOMENIANNI, and PETER VÖHRINGER — Clausius Institut für physikalische Chemie, Rheinische Friedrich-Wilhelms-Universität Bonn, Deutschland

Nitrenes have shown great potential as nitrogen-transfer reagents, owing to their high reactivity. For the same reason they are often found only as transient species and have to be prepared in-situ.^[1] Therefore, to utilize their synthetic potential to the fullest, a firm understanding of the primary processes leading up to their formation is crucial.

Herein, a set of square-planar diazide complexes^[2], [M(N₃)₂(dppe)] (dppe=1,2-Bis(diphenylphosphino)ethane, M=Ni, Pd, Pt) was studied using ultrafast UV-pump-mIR-probe and time-resolved FTIR-spectroscopy. For all complexes nitrene formation is observed, with an increase of the quantum yield dependent on the mass of the metal. Additionally an intermediate triplet state preceding the nitrene formation could be identified.

Literature: [1] T. Schmidt-Räntsch, H. Verplanck, J. N. Lienert, S.

Demeshko, M. Otte, G. P. Van Trieste, K. A. Reid, J. H. Reibenspies, D. C. Powers, M. C. Holthausen, S. Schneider, *Angew. Chem. Int. Ed.* **2022**, *61*, e202115626. [2] Hennig, H., Hofbauer, K., Handke, K., Stich, R., 1997. *Angew. Chem. Int. Ed. Engl.* **36**, 408*410.

MO 21.4 Thu 15:15 HS 3044

Time-resolved insights in the fs-range on novel Fe(III)-complexes with functional modifications — SAMIRA DABELSTEIN¹, JAKOB STEUBE², MIGUEL ANDRE ARGÜELLO CORDERO¹, FRANZISKA FENNEL¹, LENNART SCHMITZ², MARVIN KRUPP¹, CHRISTOPH VON DER OELSNITZ¹, MATTHIAS BAUER², and STEFAN LOCHBRUNNER¹ — ¹University of Rostock, Germany — ²Paderborn University, Paderborn, Germany

Precious metal-based photosensitizers in photochemistry face scarcity and extraction challenges. There's a growing shift towards Earth-abundant metal alternatives, with iron being a promising, widely available, and cost-efficient candidate. The filled t_{2g} orbitals in Fe(II)-complexes facilitate metal-to-ligand charge transfer (MLCT) upon optical excitation, while the ligand-to-metal charge transfer (LMCT) state is optimally achieved in Fe(III)-complexes owing to the partially filled t_{2g} orbitals. In this study, we present a series of emitting Fe(III)-complexes modified with functional groups. These modified variants exhibit emission from LMCT states. The lifetime and energy of the LMCT state appear to be modulated by the attachment of diverse functional groups to the ligand's backbones. Our findings, obtained through time-resolved methods, specifically femtosecond transient absorption UV-Vis spectroscopy and streak camera measurements, are presented herein. These results are thoroughly examined in the context of electronic relaxation dynamics, shedding light on the intricate processes governing the observed phenomena.

MO 21.5 Thu 15:30 HS 3044

Photophysical and photochemical investigations on a series of group VI carbonyl complexes with a meso-ionic carbene ligand — DANIEL MARHÖFER¹, PIT BODEN¹, TOBIAS BENZ², SOPHIE STEIGER¹, BIPRAJIT SARKAR², and GEREON NIEDNER-SCHATTEBURG¹ — ¹Department of Chemistry and Research Center Optimas, RPTU Kaiserslautern-Landau, Erwin-Schrödinger-Straße 52, 67663 Kaiserslautern, Germany. — ²University of Stuttgart, Chair of Inorganic Coordination Chemistry, Institute of Inorganic Chemistry, Pfaffenwaldring 55, 70569 Stuttgart, Germany.

Photo-catalysis is a well-explored field in contemporary research. It enables reactions under comparably mild conditions, that wouldn't otherwise take place. A drawback of most photo-catalysts is the requirement for rare metals as late transition metals or even rare earth metals. In order to make this field of research more sustainable and economical, it is of particular interest to develop photo-catalysts, that contain only earth-abundant metals.

In this work we present a series of Cr(0), Mo(0) and W(0) carbonyl complexes that are able to stereo-selectively cleave a CO ligand under irradiation and recombine in the dark thereafter both in the solid phase and in solution. The photophysical behavior regarding emission and excited state vibrations as well as the respective excited state lifetimes was investigated on using luminescence spectroscopy and step-scan spectroscopy. The results were compared to previously reported, isomeric complexes and backed up by DFT calculations.

MO 21.6 Thu 15:45 HS 3044

Symmetry-breaking charge transfer and intersystem crossing in copper phthalocyanine thin films — ESTHER DEL PINO ROSENDO¹, OKAN YILDIZ², TOMASZ MARZSALEK², CHARUSHEELA RAMANAN³, and PAUL W. M. BLOM² — ¹Johannes Gutenberg-Universität, Staudingerweg 7, 55128 Mainz — ²Max Planck Institut für Polymerforschung, Ackermannweg 10 55128 Mainz — ³Vrije Universiteit Amsterdam, De Boelelaan 1105, 1081 HV Amsterdam

Intermolecular interactions in π-stacked chromophores strongly influence their photophysical properties, and thereby also their function in photonic applications. Mixed electronic and vibrational coupling interactions lead to complex potential energy landscapes with competitive photophysical pathways. The photoexcited dynamics of the small molecule semiconductor CuPc are characterized in solution as well as in thin film. In the thin film case, the material can organize in two

different π -stacked architectures, α -CuPc and β -CuPc. In solution, CuPc undergoes ultrafast ISC to the triplet excited state. In the solid state, both α -CuPc and β -CuPc morphologies exhibit a mixing between Frenkel and charge-transfer excitons. We find that this mixing influences the photophysical properties differently, based on morphology. α -CuPc demonstrates symmetry-breaking charge transfer, which furthermore depends on excitation wavelength. This mechanism is not observed in β -CuPc. These results elucidate how molecular organization mediates the balance of competitive photoexcited decay mechanisms in organic semiconductors.

MO 21.7 Thu 16:00 HS 3044

Insights into exciton coupling of RNA-templated merocyanine dimer through higher-order transient absorption spectroscopy — ●AJAY JAYACHANDRAN¹, JULIA DIETZSCH², STEFAN MÜLLER¹, CLAUDIA HÖBARTNER², and TOBIAS BRIXNER¹ — ¹Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany — ²Institut für Organische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany

The synthesis of oligonucleotide scaffolds to arrange chromophores into molecular aggregates with control over the formation of their molecular excitonic states offers an exciting prospect for achieving programmable photophysics. Our study exploits the Watson-Crick base pairing interactions in a RNA double helix by incorporating a new barbituric acid merocyanine as a nucleobase surrogate via solid-phase synthesis [1]. We observe the formation of a non-fluorescent, short-lived H-aggregate.

In order to study the single- and multi-excitonic manifold of this aggregate and its associated dynamics, we use a technique that we recently developed which employs systemic intensity variation of the pump pulse in pump-probe spectroscopy to separate pure third-order and fifth-order nonlinear signals [2]. We apply this higher-order transient absorption spectroscopy for the first time on oligonucleotide scaffolds and find indications for ultrafast exciton-exciton annihilation in the H-type dimer system [1].

[1] J. Dietzsch et al., *Chem. Commun.* **59**, 7395–7398 (2023).

[2] P. Malý et al., *Nature* **616**, 280–287 (2023).

MO 21.8 Thu 16:15 HS 3044

Exciton Dynamics Pathways in a Merocyanine Dye-based Artificial Light-Harvesting Antenna — ●REBECCA FRÖHLICH¹, AJAY JAYACHANDRAN¹, ALEXANDER SCHULZ², MATTHIAS STOLTE³, FRANK WÜRTHNER^{2,3}, and TOBIAS BRIXNER¹ — ¹Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg — ²Institut für Organische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg — ³Center for

Nanosystems Chemistry (CNC), Universität Würzburg, Theodor-Boveri-Weg, 97074 Würzburg

Natural photosynthesis relies on light-harvesting systems with precisely arranged chromophore structures. We investigate the exciton dynamics in an artificial light-harvesting antenna comprised of four dipolar merocyanine chromophores, covering a broad range of the visible spectrum. The molecule shows a solvent-dependent folding-induced fluorescence enhancement previously described on a trimer structure [1]. Irrespective of excitation wavelength, the molecule fluoresces only from the lowest excitonic state, which is a sign for efficient energy transfer in the tetramer. To investigate the exciton transfer pathways we performed transient absorption measurements with selective excitation of the exciton bands and coherent 2D electronic spectroscopy. The data show downwards energy transfer via parallel energy transfer pathways. A solvent comparison reveals that the energy transfer times depend on the folding degree of the supramolecular structure.

[1] A. Schulz and F. Würthner, *Angew. Chem. Int. Ed.*, **61**, e202114667 (2022)

MO 21.9 Thu 16:30 HS 3044

Following the Chlorophyll Coupled Dynamics with High-Level Multireference X-ray Absorption Spectra — ●LENA BÄUML and REGINA DE VIVIE-RIEDLE — Department of Chemistry, LMU Munich, Germany

The omnipresent natural pigment chlorophyll is crucial for photosynthetic light-harvesting. Its nonradiative relaxation from high-energy excited states to the ground state is still not fully understood.

In an already published study we could show that the Q_x and Q_y band are strongly coupled via internal vibrations by applying grid-based wavepacket quantum dynamics on representative XMS-CASPT2 potential energy surfaces^[1]. We accounted for the coupled nuclear and electron dynamics using the NEMol ansatz developed in our group. Due to the strong coupling of the states we found the electronic coherence to be present during the entire simulation time. Transient X-ray absorption spectra (XAS) offer the possibility to resolve the ultrafast coupled dynamics experimentally. To predict the observed features we simulated XAS for the magnesium and nitrogen K-edge of chlorophyll *a* at the XMS-CASPT2 level of theory. We derived time-resolved XAS using a workflow to combine the static XAS with the coupled NEMol dynamics^[2]. Explicitly accounting for the pump pulse we could follow the nuclear wavepacket dynamics as well as predict the influence of the electronic coherence on the XAS.

[1] L. Bäuml et al., *Phys. Chem. Chem. Phys.* **24**, 27212 (2022).

[2] L. Bäuml et al., *J. Phys. Chem. A*, **127**, 9787 (2023).