

TT 32: Molecular Electronics and Excited State Properties (joint session CPP/TT)

Time: Wednesday 9:30–12:30

Location: GÖR 226

TT 32.1 Wed 9:30 GÖR 226

Strong Solvatochromism in a Two Metal Center Photocatalyst Molecule — ●MIFTAHUSSURUR HAMIDI PUTRA¹ and AXEL GROSS^{1,2} — ¹Universität Ulm Institut für Theoretische Chemie Mez-Starck-Haus Oberberghof 7 89081 Ulm Deutschland — ²Helmholtz Institute Ulm (HIU) Electrochemical Energy Storage, 89069 Ulm, Deutschland

In the theoretical study presented here, we show that the electronic and optical properties of a molecular photocatalyst can strongly depend on the solvent it is dissolved in [1]. Ground-state density functional theory and linear response time dependent density functional theory calculations are applied in order to investigate the influence of implicit solvents on the structural, electronic and optical properties of a two metal center molecular photocatalyst $[(\text{tbbpy})_2\text{Ru}(\text{tpphz})\text{PtI}_2]^{2+}$ (RuPtI_2) [2]. These calculations predict a significant dependence of the HOMO-LUMO gap of the photocatalyst on the dielectric constant of the solvent. We elucidate the electronic origins of this strong solvatochromic effect and sketch the consequences of these insights for the use of photocatalysts in different environments.

[1] M. K. Nazeeruddin, S. M. Zakeeruddin, R. Humphry-Baker, M. Jirousek, P. Liska, N. Vlachopoulos, V. Shklover, C.-H. Fischer, M. Grätzel, *Inorg. Chem.* **38**, 6298-6305 (1999).

[2] M. G. Pfeffer, T. Kowacs, M. Wächtler, J. Guthmüller, B. Dietzek, J. G. Vos, S. Rau, *Angew. Chem.* **54**, 6627-6631 (2015).

TT 32.2 Wed 9:45 GÖR 226

Dynamic Charge-Transport and Charge-Transfer Regimes for Electron-Phonon-Coupled Molecular Systems — ●MICHEL PANHANS, SEBASTIAN HUTSCH, and FRANK ORTMANN — Department of Chemistry, TU München

Different approaches for charge transport in organic solids exist but they differ significantly in the described physics of the electron-phonon coupling. In our recent work, we investigate the charge-transfer dynamics, the fading of transient localization (TL) and the formation of polarons for a large range of vibration frequencies and temperatures in the phase space of the two-site Holstein model. The combined numerical and analytical method is based on the time-domain Kubo formula of electrical conductivity to describe the highly correlated electron-phonon dynamics from femtoseconds to very large time scales, reaching nanoseconds. We identify three charge-transport regimes, which are TL, soft gating, and polaron transport. Of particular interest is the built up of correlations between the electronic motion and the nuclei manifesting in the crossover between TL and polaron transport. We find, that the transition between these two limiting cases is seamless at all temperatures and all adiabatic ratios even for the low-frequency vibrational modes that were often considered to be frozen.

TT 32.3 Wed 10:00 GÖR 226

Multichromophore Macrocycles of Perylene Bisimide Dyes as Fluorescent OLED Emitters — ●BJÖRN EWALD¹, ULRICH MÜLLER¹, PETER SPENST², PHILIPP KAGERER¹, THEODOR KAISER¹, MATTHIAS STOLTE², FRANK WÜRTHNER², and JENS PFLAUM¹ — ¹Experimental Physics VI, University of Würzburg, 97074 Würzburg — ²Institut für Organische Chemie and Center for Nanosystems Chemistry, University of Würzburg, 97074 Würzburg

Highly efficient electroluminescence from Organic Light Emitting Diodes (OLEDs) is limited by the non-radiative character of triplet states for conventional fluorophores. While fluorescent emitters benefit from high radiative recombination rates on the order of 10^9 s^{-1} , they lack from dark triplet states with lifetimes up to several μs or ms. Here we elucidate the potential of perylene bisimide macrocycles as a novel class of fluorescent OLED emitters by applying photon-correlation studies. The correlation experiments unfold additional excitonic relaxation pathways shortening the dark state lifetime for the covalently linked perylene bisimide chromophores. A trimeric chemical design leads to efficient single-photon emission from optically excited thin film samples and even under electrical operation in OLEDs. To the best of our knowledge this is the first indication of electrically-driven single-photon emission from a fluorescent molecule [1]. Therefore we consider our work to constitute an important step towards the design of state-of-the-art fluorescent OLED emitters that might also feature a high potential for application in non-classical single-photon sources.

[1] Ulrich Müller et al., *Adv. Optical Mater.* 2022, 10, 2200234.

TT 32.4 Wed 10:15 GÖR 226

A Tool Kit for Analyzing Emission Spectra of Multi-Molecular States — ●SEBASTIAN HAMMER^{1,4}, THERESA LINDERL², KRISTOFER TVINGSTEDT¹, WOLFGANG BRUETTING², and JENS PFLAUM^{1,3} — ¹Experimental Physics VI, University of Würzburg, 97074 Würzburg — ²Institute of Physics, University of Augsburg, 86135 Augsburg, Germany — ³Bayerisches Zentrum für Angewandte Energieforschung (ZAE Bayern), 97074 Würzburg — ⁴Departments for Physics and Chemistry, McGill University, Montreal, Canada

The performance of opto-electronic devices is often crucially impacted by multi-molecular excited states such as charge-transfer (CT) states or excimers. Hence, the spectroscopic analysis of these states is a common tool in the characterization of such systems. Due to the many parameters at play full quantum mechanical interpretations are tedious and therefore the analysis is often performed on a phenomenological level only. Here we present a tool kit to analyze temperature dependent emission spectra using a Franck-Condon based approach with a single effective inter-molecular vibrational mode and discuss the implications of considering different potentials for the ground and excited state harmonic oscillators [1]. Finally, we show that fundamental parameters of the potential energy landscape can be extracted from temperature dependent steady state emission spectra using the example of a tetraphenylidibenzoperiflanthene: C_{60} CT hetero-structure [2]. Funding from the DFG (Project 490894053) is gratefully acknowledged.

[1] Hammer et al., *Mater. Horiz.* (2022). doi: 10.1039/D2MH00829G

[2] Linderl et al., *Phys. Rev. Appl.* **13** 024061 (2020)

TT 32.5 Wed 10:30 GÖR 226

Singlet Fission search in polyacene molecules in gas-phase and on rare-gas clusters using ab initio methods — ●SELMANE FERCHANE and MICHAEL WALTER — Institute of Physics, University of Freiburg, Germany

Singlet fission (SF), is a spontaneous photo-excited splitting phenomenon. Where an organic chromophore dimer, converts its singlet exciton into a pair of triplet excitons. A great promise for future photon-to-current conversion of solar energy using organic materials with high efficiency. To get more insight into these processes of SF, we employed different ab initio theories and approaches in our investigation, namely, density functional theory (DFT), TD-DFT, MCTDH, and CASPT2/CASSCF. Since the spatial orientation is crucial to whether the molecule will go SF and the rate of it due to the orbital coupling of both molecules, based on recent studies. We calculate the most favorable orientation of the chromophores with the binding energies in the gas phase and adsorbed on Argon and Neon surfaces. Then we calculate the lowest-lying excited states that contribute to the singlet and triple transition plus the search for the possible conical intersection that crosses the surface potential energies.

TT 32.6 Wed 10:45 GÖR 226

Template-Designed Organic Electronics — ●KLAUS MEERHOLZ — Chemistry Department, University of Cologne, Greinstr. 4-6, 50939 Cologne, Germany

Worldwide, organic electronic devices such as OLEDs and solar cells have revolutionized the field of electronics; however, technological progress has been largely made by empirical research and development, while fundamental knowledge is often still incomplete.

This presentation will report results from the DFG-funded Research Training Group Template-Designed Organic Electronics addressing the question, how structural order influences the optoelectronic properties of pi-conjugated materials, and how these properties can be improved via the use of templates for the optimization of devices. Our approach spans all the way from the design of appropriate pi-conjugated molecular building blocks and surface-active templates, investigation of surfaces and interfaces by different spectroscopies, fabrication of optoelectronic devices, and finally theoretically modelling.

TT 32.7 Wed 11:00 GÖR 226

Optically detected magnetic resonance of TADF OLED emitters — ●PASCAL SCHADY, MONA LÖTHER, FABIAN BINDER, VLADIMIR

DYAKONOV, and ANDREAS SPERLICH — Experimental Physics VI, Julius Maximilian University of Würzburg, 97074 Würzburg

Thermally activated delayed fluorescence (TADF) is an efficient triplet harvesting mechanism for organic light-emitting diodes (OLED). Molecular TADF Donor-Acceptor type emitters are limited by low reverse intersystem crossing (rISC) rates and broad spectra, making them less suitable for potential OLED devices. In contrast, so-called multiple resonance (MR) effect emitters, are very promising as they show narrowband emission, even for deep blue wavelengths. MR-TADF emitters consist mostly of planar and rigidly bound benzyl groups with boron and nitrogen substituents for HOMO and LUMO pinning. As a result, the exchange integral is small, therefore the energy gap between singlet and triplet states is low enough to efficiently populate emissive singlet states by up-converting long-lived triplet states via thermal excitation, even at room temperature. However, many MR-TADF materials, like the DABNA-series behave differently in solution or as a solid. We therefore are investigating the spin system of those emitters by optically detected magnetic resonance (ODMR) in order to shed light on spin-dependent efficiency limiting pathways and how to address them to improve future OLED devices.

15 min. break

TT 32.8 Wed 11:30 GÖR 226

Influence of Fluorination on the Temperature Dependent Optical Transition in β - Phase ZnPc Single Crystals — •LISA SCHRAUT-MAY¹, KILIAN STRAUSS¹, SEBASTIAN HAMMER², KILIAN FRANK³, BERT NICKEL³, and JENS PFLAUM¹ — ¹Experimental Physics VI, University of Würzburg — ²Departments of Physics and Chemistry, McGill University, Montreal, Canada — ³Department of Physics, LMU Munich

The possibility of fluorination renders zinc phthalocyanine (ZnPc) an excellent model system to study the interplay between molecular packing and opto-electronic properties [1]. Here, we conduct temperature as well as polarisation dependent photoluminescence (PL) studies on β -phase ZnPc single crystals with different degrees of fluorination to modify the microscopic packing and, thus, the interaction between the molecules. For plain ZnPc an exceptionally sharp PL peak can be observed at temperatures below 100 K, which can be attributed to a superradiant enhancement [2]. Since this coherent coupling between several molecules strongly depends on the intermolecular spacing, we show, that this phenomenon can be steered by the fluorination of the molecules involved. We interpret the resulting PL signal and its temperature dependence in combination with X-ray studies by a model based on coupled excitons whose coupling is affected by the spatial anisotropy of the thermal contraction of the crystal lattice.

We thank the Bavarian research network SolTech for financial support. [1] Rödel et al., J. Phys. Chem. C (2022) [2] Hestand et al., Chem. Rev. (2018)

TT 32.9 Wed 11:45 GÖR 226

Charge Delocalization and Vibronic Couplings in Quadrupolar Squaraine Dyes — DANIEL TIMMER¹, FULU ZHENG², MORITZ GITTINGER¹, THOMAS QUENZEL¹, •DANIEL C. LÜNEMANN¹, KATRIN WINTE¹, YU ZHANG³, MOHAMED E. MADJET², JENNIFER ZABLOCKI⁴, ARNE LÜTZEN⁴, JIN-HUI ZHONG¹, ANTONIETTA DE SIO¹, THOMAS FRAUENHEIM², SERGEI TRETIK³, and CHRISTOPH LIENAU¹ — ¹University of Oldenburg, Germany — ²University of Bremen, Germany — ³Los Alamos National Laboratory, USA — ⁴University of Bonn, Germany

Squaraines are prototypical quadrupolar charge-transfer chro-

mophores. Their optical properties are often rationalized using an essential state model, predicting that optical transitions to the lowest excited state (S1) are one-photon allowed and to the next higher state (S2) are only two-photon-allowed and that vibronic coupling to high-frequency modes is greatly reduced. Here, we combine time-resolved spectroscopy techniques and quantum-chemical simulations to test and rationalize these predictions. We find the one-photon-allowed S1 and two-photon-allowed S2 states to be energetically well-separated. Also, we find small Huang-Rhys factors, especially for the high-frequency modes. The resulting concentration of the oscillator strength in a narrow spectral region around the S1 transition makes squaraines almost perfect optical two-level. Thus, these molecules and their aggregates are exceptionally interesting for e.g. strong coupling applications. [1]: Timmer, Daniel, et al., J. Am. Chem. Soc., 144, 41, 19150-19162 (2022)

TT 32.10 Wed 12:00 GÖR 226

In-operando observation of polaron formation in SAMFETs using NEXAFS spectroscopy — MANUEL JOHNSON, •ANDREAS SPÄTH, BAOLIN ZHAO, MARCUS HALIK, and RAINER H. FINK — FAU Erlangen-Nürnberg, Erlangen, Germany

We present an in-operando near-edge x-ray absorption fine structure (NEXAFS) study on p-type BTBT-based self-assembled monolayer (BTBT-SAM) films. As a 2D-model system, the BTBT-SAM offers direct electron spectroscopic insight into the active organic semiconductor layer without interfering bulk contributions. This optimized geometry allows for the first time the observation of polaronic states caused by charged species at the dielectric/organic interface using a core-level spectroscopic tool. Linear NEXAFS dichroism is employed to derive the molecular orientation of the BTBT subunit. In addition to the conventional C K-edge NEXAFS resonances, we observe modifications in the density of unoccupied states. The spectral changes are affected by the strength and polarity of the applied gate voltage. Furthermore, the related energies match the energy levels of polaronic states. Thus, we have clear indications to interpret the data in the context of polaron formation due to charge accumulation induced by the applied electric field in our ultrathin device.[1] The study has been funded by the DFG within GRK 1896 and the SolTECH initiative. [1] M. Johnson et al., Appl. Phys. Lett.121 (2022) 183503.

TT 32.11 Wed 12:15 GÖR 226

Machine learning for molecular design of organic molecules and reaction optimization — •JULIA WESTERMAJR¹, REINHARD J. MAURER², and DETLEV BELDER³ — ¹Artificial Intelligence in Theoretical Chemistry Group, Leipzig University, Germany — ²Computational Surface Chemistry Group, University of Warwick, UK — ³Analytical Chemistry, Leipzig University, Germany

High-throughput screening of reaction conditions and electronic properties of molecules plays a crucial role in chemical industry and can be facilitated by automated workflows and machine learning. However, the high combinatorial complexity of the various parameters affecting molecular properties leaves unguided searches in chemical space highly inefficient and the optimization of reactions to synthesize these molecules often fails as theoretical protocols are usually decoupled from experiments. In this talk, we will show how predictive and generative deep learning models can be combined to theoretically design new molecules with potential relevance to organic electronics [1]. Further, we will present how these tools can be coupled with experiments to enable automated micro-laboratories [2] for targeted chemical synthesis. [1] JW et al. Nat. Comp. Sci, in press (2023). [2] R. J. Beulig et al., Lab Chip 17, 1996 (2017).