

CPP 39: Molecular Electronics and Excited State Properties

Time: Thursday 11:30–13:00

Location: H38

CPP 39.1 Thu 11:30 H38

Fluorinated Acenes: Controlling Molecular Electronic Levels, Crystalline Phases and Optoelectronic Properties — •DANIEL BISCHOF¹, PHILIPP E. HOFMANN², MATTHIAS W. TRIPP², MARC ZEPICHAL³, SEBASTIAN ANHÄUSER¹, TOBIAS BREUER¹, SERGEI I. IVLEV², MARINA GERHARD¹, ANDREAS TERFORT³, ULRICH KOERT², and GREGOR WITTE¹ — ¹Fachbereich Physik, Philipps-Universität Marburg — ²Fachbereich Chemie, Philipps-Universität Marburg — ³Goethe Universität Frankfurt

Acenes serve as prototypical molecular materials to study structure-property relationships. Here, we systematically analyze the influence of the acene length and the degree of fluorination on their structure and optoelectronic properties [1–3]. Our results show that the optical gap decreases with increasing acene length, while the degree of fluorination determines the precise energy levels of the frontier orbitals HOMO and LUMO, whereas the optical gap is barely affected upon fluorination. Partial fluorination also influences the molecular electrostatic potential (MEP) and leads to a change in the molecular packing from herringbone packing for pristine and perfluorinated acenes to a planar stacking motif. These structural changes also affect the photoluminescence properties and induce a red-shifted PL for the stacked molecules due to excimer formation. The presented insights are not limited to acenes, but can be extended to other π -conjugated systems.

[1] P. E. Hofmann, et al. *Angew. Chem. Int. Ed.* 59, 16501 (2020).

[2] D. Bischof et al. *J. Phys. Chem. C* 125, 19000 (2021).

[3] D. Bischof et al. *Chem. Eur. J.* 28, e202103653 (2022).

CPP 39.2 Thu 11:45 H38

Time-resolved spectroscopy study of the dynamics of charge transfer processes in strongly interacting organic donor/acceptor compounds — •NICO HOFEDITZ¹, CHRISTOPH P. THEURER², JULIAN HAUSCH², KATHARINA BROCH², WOLFRAM HEIMBRODT¹, and MARINA GERHARD¹ — ¹Department of Physics, Philipps-Universität Marburg, Germany — ²Institut für Angewandte Physik, Universität Tübingen, Germany

Doping of organic semiconductors with strong acceptor molecules is an effective way to tailor their electronic properties. Here, we investigate the photoexcitation dynamics of blends of tetracene and the strong acceptor F4-TCNQ to better understand how acceptors alter the transport of charge carriers and excitons. The mixtures feature a phase of relatively pure tetracene as well as an intimately mixed phase. In the mixed phase donor and acceptor molecules form charge transfer complexes that efficiently quench excitons from the pure phases. That leads to faster photoluminescence dynamics in the blends with respect to neat tetracene. We investigate the low temperature photoluminescence through global analysis and find constrained dynamics in the blends which we attribute to localization effects and energetic disorder in the tetracene domains.

CPP 39.3 Thu 12:00 H38

Ultrafast excited states dynamics of two orthogonal molecular photoswitches — •TANJA SCHMITT¹, LI-YUN HSU², EVA BLASCO², and PETRA TEGEDER¹ — ¹Physical Chemistry, Ruprecht-Karls-Universität Heidelberg — ²Organic Chemistry, Ruprecht-Karls-Universität Heidelberg

Molecular photoswitches are widely used in physics, chemistry, biology and material sciences. The use of multiple photoswitches at one time opens diverse opportunities for further improved and more complicated systems. This requires orthogonal addressability of the photoswitches and ideally reversible processes. Herein, we report a mixture of two reversible and orthogonal photoswitches which could potentially be used in four-dimensional printing. We report the first study of their ultrafast excited state dynamics when they are addressed orthogonally as well as simultaneously to gain insight in their interaction. In addition, the environmental influence of the excited state dynamics of the orthogonal photoswitches is examined using different solvents as well as films.

CPP 39.4 Thu 12:15 H38

Charge Transfer and Singlet Fission in Pentacene/Acceptor thin films — •MARTIN RICHTER¹, CHRISTOPH THEURER², DEBKUMAR RANA^{1,3}, KATHARINA BROCH², and PETRA TEGEDER^{1,3} —

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Singlet fission (SF) is a process where a singlet excited state is converted into two triplet excited states. Since SF is exothermic in pentacene (PEN), it is an excellent material to investigate charge transfer (CT) interactions with electron acceptors. Here, stacked bi-layers of PEN either with 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4-TCNQ) or 2,2'-(perfluoronaphthalene-2,6-diylidene)dimalononitrile (F6-TCNNQ) were investigated with transient absorption spectroscopy. The experiments show formation of triplet pairs, due to the SF process with a slightly slower time constant compared to the pure PEN. Subsequently a separation of the correlated triplet pair can be observed, a process that has been identified also in PEN thin films. A drastic reduction of the triplet lifetime is extracted with both acceptors. Further, evidence for diffusion of excitons to the interface followed by charge formation is found for layers with F4-TCNQ, supported by the shifting of an absorption band, caused by electric fields.

CPP 39.5 Thu 12:30 H38

Understanding charge transfer excitations in Bacteriochlorophyll dimers from first principles — •ZOHREH HASHEMI¹, MATTHIAS KNODT¹, and LINN LEPPERT^{1,2} — ¹Institute of Physics, University of Bayreuth, Germany — ²MESA+ Institute for Nanotechnology, University of Twente, Netherlands

Bacteriochlorophyll (BCL) molecules are the main pigments driving the primary excitation and charge transfer processes in photosynthetic bacteria. They are organized in highly coordinated multichromophoric complexes, embedded in protein, guaranteeing an efficient transfer of excitation energy from the light harvesting antennae to the reaction center where a charge transfer excitation triggers. In this contribution we focus on the electronic and excited state structure of BCL monomers and dimers found in the reaction center and light harvesting apparatus of the purple bacterium *Rhodobacter sphaeroides*. We assess the accuracy of ab initio GW+Bethe-Salpeter equation approach for BCL monomers considering a wide range of excitation energies, and find excellent agreement with experimental data and correlated wavefunction-based approaches. We also discuss notable differences to results from state-of-the-art time-dependent density functional theory, which can be traced back to the treatment of electron-hole interactions in both methods [1]. For dimeric systems we show that the energy and character of charge transfer excitations is strongly affected by distance and orientation of the BCL molecules, providing an intuitive understanding for the role of these excitations in different parts of the photosynthetic apparatus.

CPP 39.6 Thu 12:45 H38

Temperature Dependent Optical Transition in Zinc Phthalocyanine Single Crystals — •LISA SCHRAUT-MAY¹, SEBASTIAN HAMMER¹, KILIAN FRANK², BERT NICKEL², and JENS PFLAUM^{1,3} — ¹Experimental Physics VI, Julius Maximilian University, 97074 Würzburg — ²Department of Physics and Center for Nano Science, Ludwig Maximilian University, 80539 Munich — ³Bavarian Center for Applied Energy Research, 97074 Würzburg

By its various polymorphs, Zinc Phthalocyanine (ZnPc) serves as an excellent model system to study the interplay between molecular packing on microscopic length scales and the resulting photophysical properties [1]. Here, we address the dependence of the excitonic coupling on the underlying crystal structure of the thermodynamically stable ZnPc β -phase. For this purpose, we conducted complementary temperature dependent X-ray diffraction as well as polarization dependent photoluminescence (PL) studies on ZnPc single crystals. By means of the PL signals spectral characteristics we observed a continuous transition from a J- into an H-aggregated state between 300 K and 100 K. Remarkably, below 100 K an exceptionally sharp PL peak evolves being indicative for the formation of a superradiant J-aggregate. As there is no indication for a discrete structural phase transition, we interpret the resulting PL signal in this temperature range by a model of vi-

tronically coupled excitons steered by the gradual anisotropic thermal contraction of the crystal lattice [2]. We thank the Bavarian research

network SolTech for financial support. [1] Hammer et al., Appl. Phys. Lett. (2019) [2] Hestand et al., Chem. Rev. (2018)