

## CPP 3: Molecular Electronics and Excited State Properties

Time: Monday 9:30–13:00

Location: H13

## Invited Talk

CPP 3.1 Mon 9:30 H13

**Tailoring the Excited State Energy Landscape in Supramolecular Nanostructures** — ●RICHARD HILDNER — Soft Matter Spectroscopy, University of Bayreuth, Bayreuth, Germany — Zernike Institute for Advanced Materials, University of Groningen, Groningen, Netherlands

Application of organic macromolecules in molecular electronics and nanophotonics requires their well-defined assembly into nano- and mesoscale structures to allow for efficient energy and/or charge transport. Here we demonstrate robust self-assembly of so-called carbonyl-bridged triarylaminines (CBT) into micrometre-long objects driven by specific supramolecular motifs. Depending on the solvent we are able to prepare isolated supramolecular nanofibres, in which the CBT molecules are cofacially stacked (H-aggregate), or to prepare well-defined bundles of such nanofibres. Combining optical spectroscopy with electron microscopy and numerical modelling, we find that isolated nanofibres possess a high degree of structural order. In turn, this results in a high degree of electronic order in the electronically excited states. In contrast, in nanofibre bundles the structural and electronic order is significantly less pronounced. We show that this difference in order has substantial impact on the transport of excitation energy: While isolated nanofibres exhibit long-range energy transport of several micrometres, in nanofibre bundles this is not the case. Hence, the solvent allows to tune the excited state energy landscape of nanofibres, which in turn allows to control the transport characteristics of excitation energy along nanofibres.

CPP 3.2 Mon 10:00 H13

**Controlling H- and J-type electronic coupling in single deterministic conjugated polymer aggregates** — ●THERESA EDER<sup>1</sup>, CHRISTOPH ALLOLIO<sup>2</sup>, DOMINIK HORINEK<sup>2</sup>, SIGURD HÖGER<sup>3</sup>, JAN VOGELSANG<sup>1</sup>, and JOHN M. LUPTON<sup>1</sup> — <sup>1</sup>Institut für Experimentelle und Angewandte Physik, Universität Regensburg, Germany — <sup>2</sup>Institut für Physikalische und Theoretische Chemie, Universität Regensburg, Germany — <sup>3</sup>Kekulé-Institut für organische Chemie und Biochemie, Universität Bonn, Germany

The electronic coupling in conjugated polymers, which impacts the spectroscopic behavior tremendously, can be explained in the theoretical framework of H- and J-aggregation between neighboring chromophoric units. We investigate custom-synthesized model polymers and oligomers and show how the distance between chains impacts the coupling type [1]. Based on the work on single polymer aggregates, we intramolecularize aggregation by designing single dimers and trimers with a fixed spatial distance of the conjugated units. Here, we are also able to demonstrate, in combination with molecular dynamics and TDDFT calculations, that strong H-type coupling occurs in ordered oligomers at close spacings, whereas disorder and increased spacing quenches coupling [2]. Further, the examination of single-molecule spectra allows us to show how an increase in the dimer length with similar chromophore distance gives rise to increased J-type attributes such as spectral narrowing and reduced vibronic coupling.

[1] T. Eder et al., *Nature Commun.* 8, 1641 (2017)[2] C. Allolio et al., *J. Phys. Chem. B* 122, 6431 (2018)

CPP 3.3 Mon 10:15 H13

**Controlling Exciton Dynamics in Tetracene-Derivatives by Covalent Bonding of Two Chromophores** — ●MAXIMILIAN FRANK<sup>1</sup>, ULRICH MÜLLER<sup>1</sup>, LENA ROOS<sup>2</sup>, ANKE KRUEGER<sup>2</sup>, and JENS PFLAUM<sup>1,3</sup> — <sup>1</sup>Experimental Physics VI, Julius Maximilian University of Würzburg, 97074 Würzburg — <sup>2</sup>Institute of Organic Chemistry, Julius Maximilian University of Würzburg, 97074 Würzburg — <sup>3</sup>ZAE Bayern, 97074 Würzburg

For an efficient operation of optoelectronic devices it is inevitable to control the photodynamics and, thus, the relevant loss channels like charge transfer formation or singlet fission (SF). In case of the latter, the excited singlet state decays into two triplet states of lower energy located on neighboring chromophores. Tetracene (Tc) is a model system to study this process and has motivated us to prove by rational design, here the covalent linking of two Tc chromophores, the effect of molecular packing on the optical properties and, in particular, on SF. By a comparative study on neat Tc and ditetracene (DTc) bulk crystals as well as anthracene crystals doped by the two entities at the single

molecule level, different excitonic states can be identified together with the influence of the local environment and temperature. Quantities like spectral selective fluorescence lifetime, photoluminescence and absorption spectra as well as quantum efficiency are presented for each of the sample types studied, showing, as a key result, that SF is suppressed in DTc crystalline aggregates. Therefore, a model for the excitation energy landscape of DTc single crystals can be deduced and highlights the effect of the additional covalent bond on the photodynamics.

CPP 3.4 Mon 10:30 H13

**Ultrafast excited state relaxation monitored by single molecule photon statistics** — ●JAKOB SCHEDLBAUER<sup>1</sup>, PHILIPP WILHELM<sup>1</sup>, MARIA-ELISABETH FEDERL<sup>1</sup>, FLORIAN HINDERER<sup>2</sup>, SIGURD HÖGER<sup>2</sup>, LENNART GRABENHORST<sup>3</sup>, PHILIP TINNEFELD<sup>3</sup>, JAN VOGELSANG<sup>3</sup>, SEBASTIAN BANGE<sup>1</sup>, and JOHN M. LUPTON<sup>1</sup> — <sup>1</sup>Universität Regensburg, Germany — <sup>2</sup>Universität Bonn, Germany — <sup>3</sup>LMU München, Germany

A new experimental approach is presented to monitor ultrafast excited state deactivation combining single molecule fluorescence spectroscopy (SMS) with a pump-probe-like excitation scheme. In the simplest way a single molecule can be described as a two level system and therefore can emit only one single photon after a given excitation pulse, a phenomenon referred to as photon antibunching. By introducing a second excitation pulse after a variable time lag the probability for reexciting the system and generating a second photon is a function of the excited state lifetime. A Hanbury-Brown-Twiss based detection setup enables us to measure the probability for the emission of multiple photons after a given excitation cycle.

This technique overcomes the limitation of conventional fluorescence based lifetime measurements such as time-correlated single-photon counting, which is constrained by finite detector instrument response function. We resolve dynamical single molecule processes like the intramolecular energy transfer in an acceptor-donor-acceptor system (13 ps) as well as ultrafast enhanced PL of Cy7 dyes coupled to a plasmonic antenna structure (20 ps).

CPP 3.5 Mon 10:45 H13

**Simultaneous Singlet-Singlet and Triplet-Singlet Förster Transfer** — ●ANTON KIRCH, MAX GMELCH, and SEBASTIAN REINEKE — Dresden Integrated Center for Applied Physics and Photonic Materials (IAPP), Technische Universität Dresden, 01187 Dresden, Germany

We present our study of Förster resonant energy transfer (FRET) for the interesting case using a biluminescent donor material. FRET is used as spectroscopic ruler in various research fields and also determines many photonic and optoelectronic applications on the nanoscale. A biluminescent organic molecule is one that shows both fluorescence and phosphorescence at room temperature, where the latter is only observed under special conditions, which are currently widely explored in material research. The time dynamics of such a biluminophore is very special, spanning from nanoseconds-lifetime fluorescence to seconds-lifetime phosphorescence.

Here, we show that such a biluminescent donor can transfer its energy of both singlets and triplets to a fluorescent donor in the exact same framework of FRET. For both singlet and triplet energy transfer, we separately determine the nanoscale range (< 10 nm). The unified observation and description of singlet and triplet FRET from the very same molecular origin (same donor) has not been discussed in literature before. Importantly, our study validates Förster's theory on a single system over eight orders of magnitude in respective excited state lifetimes.

CPP 3.6 Mon 11:00 H13

**Polarized absorbance and Davydov splitting in bulk and thin-film pentacene polymorphs** — ●CATERINA COCCHI<sup>1</sup>, TOBIAS BREUER<sup>2</sup>, GREGOR WITTE<sup>2</sup>, and CLAUDIA DRAXL<sup>1</sup> — <sup>1</sup>Physics Dept. and IRIS Adlershof, Humboldt-Universität zu Berlin, Germany — <sup>2</sup>Faculty of Physics, Philipps-Universität Marburg, Germany

Pentacene is one of the most studied organic materials but a number of issues related to it are still debated. One of them concerns the role of polymorphism and its effects on the lowest-energy excitations, appearing in the visible region and being subject to a sizable Davydov

splitting. We address this problem in a combined theoretical and experimental work, where the electronic and optical properties of three pentacene phases (two bulk polymorphs and the thin-film phase) are investigated. Optical spectra computed from many-body perturbation theory are compared with the polarization-resolved absorbance. In this way, the two Davydov components of the first exciton are identified along with the optical fingerprints of each considered phase. All polymorphs exhibit common features at the absorption onset, while phase-dependent characteristics appear only above 2 eV. We discuss the character of the lowest-lying singlet and triplet excitons, highlighting the contributions from the electronic bands as well as the role of electron-hole interaction and local-field effects [1].

[1] C. Cocchi T. Breuer, G. Witte, and C. Draxl Phys. Chem. Chem. Phys. DOI: 10.1039/C8CP06384B (2018).

### 15 min. break

CPP 3.7 Mon 11:30 H13

**Temperature Dependent Photoluminescence Studies on Zinc Phthalocyanine Single Crystals** — ●LARISSA LAZAROV<sup>1</sup>, SEBASTIAN HAMMER<sup>1</sup>, and JENS PFLAUM<sup>1,2</sup> — <sup>1</sup>Experimental Physics VI, Julius Maximilian University of Würzburg, 97074 Würzburg — <sup>2</sup>ZAE Bayern, 97074 Würzburg

Zinc-phthalocyanine (ZnPc) has been one of the most studied materials in organic solar cells, due to its high photostability, electronic tunability and superior opto-electronic properties compared with other metal-phthalocyanines [1]. Remarkably, the microscopic photophysical processes in ordered ZnPc aggregates have not been studied in great detail so far. For this purpose, we grew ZnPc single crystals via gradient sublimation and confirmed their crystallographic  $\beta$ -phase by X-ray diffraction. Temperature dependent photoluminescence (PL) studies have been performed from 4 to 330 K. Below 100 K the radiative 0-0 vibronic transition consists of two narrow lines with a FWHM of about 20 meV, respectively. The emission intensity in this temperature range indicates superradiance accompanied by exciton delocalization over several molecules according to Spano's method [2]. Above 100 K, thermally activated aggregate emission appears to be the dominant process in PL enhancement by up to one order of magnitude at 330 K. We discuss the superradiant behavior in respect to its dependence on polarization and excitation power and shed light on the microscopic processes leading to the emission behavior at elevated temperatures.

[1] Brendel et al., *Adv. Funct. Mater.*, **25**, 2015

[2] Spano, F.C., Yamagata, H., *JPCB* **115**, 5133-5143, 2011

CPP 3.8 Mon 11:45 H13

**Programmable transparent organic luminescent tags** — ●MAX GMELCH, HEIDI THOMAS, FELIX FRIES, and SEBASTIAN REINEKE — Dresden Integrated Center for Applied Physics and Photonic Materials (IAPP), Technische Universität Dresden, 01187 Dresden, Germany

A novel approach for organic luminescent labeling is shown, providing unmatched image resolution (>700 dpi) combined with fast and multiple (>40 cycles) printing onto and erasing from various substrates in any shape or size. These ultrathin, fully transparent and flexible organic tags contain highly available materials only and are easy to process. The material system consists of an organic biluminescent emitter, embedded into a PMMA host matrix and covered by an oxygen barrier layer. It shows room temperature phosphorescence (RTP), which in general is quenched by molecular oxygen. However, by illuminating with ultraviolet light, this molecular oxygen locally vanishes at the irradiated spots, enabling RTP at defined spots. Further, by illuminating with infrared light, the system can be refilled with oxygen leading to quenching of the RTP again. Therefore, any luminescent pattern can be written into and erased from the tag without contact or the use of any ink. Using light only, this new technology offers the possibility of invisible on-demand information readout.

CPP 3.9 Mon 12:00 H13

**Absence of Charge Transfer States at Crystalline Perfluoropentacene/Pentacene Interfaces** — ●SEBASTIAN HAMMER<sup>1</sup>, CLEMENS ZEISER<sup>2</sup>, KATHARINA BROCH<sup>2</sup>, and JENS PFLAUM<sup>1,3</sup> — <sup>1</sup>Experimental Physics VI, Julius Maximilian University of Würzburg, 97074 Würzburg — <sup>2</sup>Institute for Applied Physics, University of Tübingen, 72076 Tübingen — <sup>3</sup>ZAE Bayern, 97074 Würzburg

The formation of charge transfer (CT) states plays an important role in charge separation and impacts the efficiency of organic photodetectors and photovoltaics. Pentacene:Perfluoropentacene (P:PFP) has

been largely studied in mixed films as a prototypical CT system by its suited donor/acceptor (D/A) energy levels [1][2]. However, the role of molecular orientation on charge transfer has not been elucidated, so far. For this purpose, we used heteroepitaxial growth of PFP on P (001) crystal interfaces to achieve long-range ordered D/A heterojunctions of edge-on molecular orientation as confirmed via X-ray diffraction. By means of temperature dependent cw fluorescence spectroscopy and *in-situ* differential reflectance spectroscopy we determined the optical characteristics of the PFP/P thin films and demonstrate the absence of CT state formation at the generic (001) edge-on crystalline interface. We discuss these findings with respect to possible implementation in organic solar cells where the suppression of strongly bound CT states at D/A heterointerfaces yields an increase in open circuit voltage, and thus in device performance.

[1] K. Broch et al., *Phys. Rev. B* **83**, 245307 (2011)

[2] T. Breuer, G. Witte, *J. Chem. Phys.* **21**, 138 (2013)

CPP 3.10 Mon 12:15 H13

**Interplay between intra- and inter-molecular charge transfer in the optical excitations of J-aggregates** — ●MICHELE GUERRINI<sup>1,2,3</sup>, CATERINA COCCHI<sup>2</sup>, ARRIGO CALZOLARI<sup>3</sup>, DANIELE VARSANO<sup>3</sup>, and STEFANO CORNI<sup>3,4</sup> — <sup>1</sup>Dept. FIM, Univ. of Modena and Reggio Emilia, Italy — <sup>2</sup>Dept. of Physics and IRIS Adlershof, Humboldt Universität zu-Berlin, Germany — <sup>3</sup>CNR Nano, Centro S3, Modena, Italy — <sup>4</sup>Dept. Chem. Scienc., Univ. of Padova, Italy

Molecular J-aggregates formed by push-pull chromophores have appealing optical properties which are dominated by collective and supramolecular effects, as recently demonstrated from first principles [1]. Here, we investigate the character of the optical excitations from many-body perturbation theory, focusing on the interplay between intra- and inter-molecular interactions. We find that the most intense excitation which dominates the spectral onset (the so-called J-band) exhibits a combination of intra-molecular charge transfer, coming from the push-pull character of the constituting dyes, and inter-molecular charge-transfer, due to the dense molecular packing which favors wavefunction delocalization. Within the J-band we also reveal the presence of a pure inter-molecular charge-transfer excitation. Our results [2] shed light into the microscopic character of optical excitations in J-aggregates and offer new perspectives for understanding the nature of collective excitations in organic molecular solids.

[1] M. Guerrini; A. Calzolari; S. Corni ACS Omega 2018, 3 (9), 10481-10486. [2] M. Guerrini; C. Cocchi; A. Calzolari; D. Varsano; S. Corni submitted (2018).

CPP 3.11 Mon 12:30 H13

**Differentiation between the optical signatures of aggregates and of isolated chains in doped P3HT solutions** — ●AHMED E. MANSOUR<sup>1</sup>, DOMINIQUE LUNGWITZ<sup>1</sup>, THORSTEN SCHULTZ<sup>1</sup>, ANDREAS OPITZ<sup>1</sup>, and NORBERT KOCH<sup>1,2</sup> — <sup>1</sup>Institut für Physik & IRIS Adlershof, Humboldt Universität zu Berlin, Germany — <sup>2</sup>Helmholtz Zentrum Berlin für Materialien und Energie GmbH, Germany

Molecular doping of Poly(3-hexylthiophene-2,5-diy) (P3HT) results in the formation of polarons as the main charge carriers. Charged polymer segments can be identified by optical absorption spectroscopy.[1,2] Furthermore, molecular doping typically may lead to aggregation of P3HT and the dopant already in the solution, which alters the film morphology.[3,4] Herein, we compare the optical signatures of doped aggregates and doped single chains in solution. Their relative size is compared by filtering doped suspensions for different absolute concentrations and dopant ratios. We find that doped single chains exhibit absorption features at 1.5 eV and 0.6 eV. For doped aggregates, the peak at higher absorption energy is split into two absorption features at 1.3 eV and 1.65 eV. Further, we show that the size of dopant induced aggregation increases as a function of absolute concentration and dopant ratio. Doped P3HT suspensions are shown to comprise both doped species, with the aggregates exhibiting a larger dopant loading.

[1]Bredas, J. L. et al., *Acc. Chem. Res.* 1985, 18, 309. [2]Heimel, G., *ACS Cent. Sci.* 2016, 2, 309. [3]McFarland, F. M. et al., *J. Phys. Chem. C* 2017, 121, 4740. [4]Jacobs, I. E. et al, *J. Mater. Chem. C* 2016, 4 (16), 3454.

CPP 3.12 Mon 12:45 H13

**What is the impact of the donor length on the electronic and optical properties of charge-transfer complexes?** — ●ANA M VALENCIA and CATERINA COCCHI — Physics Department, Humboldt-Universität zu Berlin und IRIS Adlershof

The size ratio between donor and acceptor moieties in organic semi-

conductors is known to effectively influence the doping mechanism [1]. Here, we investigate a series of charge transfer complexes formed by oligothiophene molecules of increasing length doped by the acceptor F4TCNQ. Using hybrid DFT as a starting point, we assess the electronic and optical properties of these systems from many-body perturbation theory (GW and the Bethe-Salpeter equation). We find that the frontier orbitals (HOMO and LUMO) are hybridized in all complexes, while the distribution of deeper occupied and higher virtual states depend on the nT length. The first bright excitation is domi-

nated by the HOMO-LUMO transition occurring approximately at the same energy in all systems. At increasing donor length, higher-energy peaks exhibit different character depending on the donor conjugation length [2]. We also consider how the relative concentration of donor and acceptor molecules impacts these properties. The rationale offered by our results contributes to clarify the excitation processes in organic donor/acceptor complexes. [1] H. Mendez, et al., Nat. Comm. 6, 8560 (2015). [2] A.M. Valencia and C. Cocchi submitted (2018).