

CPP 26: Organic Electronics and Photovoltaics: OPV I (joint session CPP, HL, TT)

Time: Tuesday 14:00–16:00

Location: C 130

Invited Talk

CPP 26.1 Tue 14:00 C 130

Ultrafast Coherent Charge Transfer in Solar Cells and Artificial Light Harvesting Systems — ●CHRISTOPH LIENAU¹, EPHRAIM SOMMER¹, ANTONIETTA DE SIO¹, RALF VOGELGESANG¹, MARGHERITA MAIURI², GIULIO CERULLO², ANGEL RUBIO³, CARLO A. ROZZI⁴, and ELISA MOLINARI⁴ — ¹Carl von Ossietzky University, Oldenburg, Germany — ²Politecnico di Milano, Milano, Italy — ³Universidad del País Vasco, San Sebastian, Spain — ⁴Dipartimento di Scienze Fisiche, Modena, Italy

To elucidate the fundamental microscopic processes in solar energy conversion, we have recently combined coherent femtosecond spectroscopy and first-principles quantum dynamics simulations [1,2] and have used this approach to explore the primary photoinduced electronic charge transfer in two prototypical structures: (i) a caroteneporphyrin-fullerene triad, an elementary component for an artificial light harvesting system [2] and (ii) a polymer:fullerene blend as a model for an organic solar cell [1].

Our results provide strong evidence that in both systems, at room temperature, the driving mechanism of the primary step within the current generation cycle is a quantum-correlated wavelike motion of electrons and nuclei on a timescale of few tens of femtoseconds. They suggest that the strong coupling between electronic and vibrational degrees of freedom is of key importance for the dynamics and yield of the charge separation process. Here, I will discuss our most recent experimental and theoretical findings. [1] S. M. Falke et al., *Science* 344, 6187 (2014). [2] C. A. Rozzi et al., *Nature Comm.* 4, 1602 (2013)

CPP 26.2 Tue 14:30 C 130

Calculation of exciton dissociation rates in ordered and disordered 2D model organic photovoltaic interfaces — ●HECTOR VAZQUEZ¹ and ALESSANDRO TROISI² — ¹Inst. of Physics, Academy of Sciences of the Czech Rep., CZ — ²Dept. of Chemistry and Centre of Scientific Computing, University of Warwick, UK

The efficient generation of free charges from incident light in organic photovoltaic cells has been studied extensively but is not yet well understood. In order to separate, electron and hole have to overcome the Coulomb attraction and several mechanisms have been proposed. In particular, 'hot' excitons having excess energy have received a lot of attention but no consensus yet exists [1].

In this talk, I will introduce a method to calculate exciton dissociation rates [2] and will describe its application to 2-Dimensional model organic photovoltaic interfaces. The method uses Green's functions within a widely applicable model Hamiltonian of donor/acceptor interfaces with and without disorder. Initial states are Frenkel excitons while final states are Charge-Transfer (CT) states. I will present results for the generation rates of CT states where I will highlight the importance of disorder and the delocalization of the excitonic wavefunctions. Excitons dissociate into 'hot' CT states with partially separated charges, where electron and hole are located far from the interface.

1) A. A. Bakulin et al., *Science* 335, 1340 (2012), A. E. Jailaubekov et al., *Nat. Mater.* 12 66 (2013), G. Grancini et al., *Nat. Mater.* 12 29 (2013), K. Vandewal et al., *Nat. Mater.* 13 63 (2013).

2) H. Vazquez, A. Troisi, *Phys. Rev. B* 88, 205304 (2013).

CPP 26.3 Tue 14:45 C 130

Charge separation at C₆₀/P3HT and P3HT/ZnO interfaces probed by femtosecond time-resolved second harmonic generation measurements — ●MARC HÄNSEL¹, MICHAEL SCHULZE¹, YUNUS SEVINCHAN², YANA VAYNZOR², and PETRA TEGEDER¹ — ¹Physikalisch-Chemisches Institut, Heidelberg, Germany — ²Centre of Advanced Materials, Heidelberg, Germany

A deeper understanding of the process of ultrafast charge transfer and separation at donor/acceptor interfaces is a prerequisite for improvement of organic and hybrid solar cells. Time-resolved second harmonic generation (TR-SHG) with femtosecond temporal resolution was used to investigate different donor/acceptor interfaces. With this intrinsically interface sensitive technique we were able to monitor the charge transfer dynamics of the well-defined single heterojunctions C₆₀/P3HT and P3HT/ZnO. In addition some modifications via cesium doping were made to the ZnO/P3HT interface. At the C₆₀/P3HT interface a pump energy dependent ultrafast charge transfer state with a population-time of 320fs has been observed.

CPP 26.4 Tue 15:00 C 130

Modelling charge transfer in Polymer/SWNT/PCMB hybrid systems — ●LIVIA GLANZMANN, DUNCAN MOWBRAY, and ANGEL RUBIO — Nano-bio Spectroscopy Group and ETSF Scientific Development Centre, Universidad del País Vasco UPV/EHU, Av. Tolosa 72, E-20018 San Sebastian, Spain

One way to increase power conversion efficiencies of organic photovoltaic devices (OPVs) is to optimize the electron donor (D) acceptor (A) materials. The level alignment of the frontier orbitals at the D-A heterojunction interface is important for an efficient charge transfer. Since the first heterojunction OPV, consisting of 3-alkylpolythiophene (P3HT) and Fullerene, several combinations of D-A materials were tested. As well, carbon nanotubes were introduced, which increased the efficiency of such multi-component systems. Still, the electronic processes within such systems are not well understood. To shed light on this subject, we simulate photovoltaic processes occurring in selected sets of P3HT-based-Polymer/SWNT or PCBM heterojunctions. As a first step, we create the excited states within the donor materials by performing TDDFT calculations and extract the electron density of the exciton. Then, we use the delta SCF approach to study the D-A electron transfer. On top, we calculate the probability of an electron passing the D-A interface and being transported through a nanotube by performing GOW0 calculations. All these results show the effect of certain types of D-A material, as well of their level alignment, on the efficiency of OPVs.

CPP 26.5 Tue 15:15 C 130

Photoinduced Dynamics of Charge Separation: from Photoynthesis to Polymer-Fullerene Bulk-Heterojunctions — ●ANDREAS SPERLICH¹, OLEG G. POLUEKTOV², JENS NIKLAS², and VLADIMIR DYAKONOV^{1,3} — ¹Experimental Physics VI, Julius Maximilian University of Würzburg, 97074 Würzburg — ²Chemical Sciences and Engineering Division, ANL, Argonne, Illinois 60439, USA — ³ZAE Bayern, 97074 Würzburg

Understanding charge separation and charge transport is crucial for improving the efficiency of organic solar cells. This is due to the excitonic nature of their active media, based on organic molecules, serving as both a light absorbing and transport layer. Charge transfer (CT) states play an important role, being intermediate for free carrier generation and charge recombination. Here, we use light-induced electron paramagnetic resonance (EPR) spectroscopy to study the charge transfer dynamics in composites of the polymers P3HT, PCDTBT, and PTB7 with the fullerene derivative PC₆₀BM. Transient EPR measurements show strong spin-polarization patterns for all polymer-fullerene blends, confirming predominant generation of singlet CT states. These observations allow a comparison with charge separation processes in molecular donor-acceptor systems, as found in natural and artificial molecular photosynthetic systems and clarification of the initial steps of sequential charge transfer in organic photovoltaic (OPV) materials. The detection of strong electron spin-polarization in OPV materials points out to the significance of spin dynamics for the efficient functioning of solar cell devices.

CPP 26.6 Tue 15:30 C 130

Sub-ns Triplet State Formation in PSBTBT:PC70BM and PCPDTBT:PC60BM Photovoltaic Blends — FABIAN ETZOLD¹, IAN HOWARD^{1,2}, and ●FRÉDÉRIC LAQUAI¹ — ¹Max Planck Research Group for Organic Optoelectronics, Max Planck Institute for Polymer Research, D-55128 Mainz, Germany — ²Institute of Microstructure Technology (IMT), Karlsruhe Institute of Technology (KIT), D-76344 Eggenstein-Leopoldshafen, Germany

The excited state dynamics in low-bandgap polymer:fullerene blends using the donor-acceptor copolymers PCPDTBT and its silicon-substituted analogue PSBTBT are investigated by femto- to microsecond broadband Vis-NIR transient absorption (TA) pump-probe spectroscopy. The TA experiments and analysis of the TA data by multivariate curve resolution (MCR-ALS) reveal that after exciton dissociation and free charge formation is completed, fast sub-nanosecond non-geminate recombination occurs and leads to a substantial population of the polymer's triplet state. The extent to which triplet states are formed depends on the initial concentration of free charges, which itself is controlled by the microstructure of the blend, especially in case of

PCPDTBT:PC60BM. Interestingly, PSBTBT:PC70BM blends show a higher charge generation efficiency, but less triplet state formation at similar free charge carrier concentrations. This indicates that the solid-state morphology and interfacial structure of PSBTBT:PC70BM blends reduce non-geminate recombination and thus triplet state formation, leading to increased device performance compared to optimized PCPDTBT:PC60BM blends.

CPP 26.7 Tue 15:45 C 130

Triplet Exciton Formation in High-Efficiency Donor-Acceptor Photovoltaic Blends — ●STEFAN VÄTH¹, HANNES KRAUS¹, ANDREAS BAUMANN², KRISTOFER TVINGSTEDT¹, ANDREAS SPERLICH¹, VLADIMIR DYAKONOV^{1,2}, JOHN LOVE³, and THUC-QUYEN NGUYEN³ — ¹Experimental Physics VI, Julius Maximilian University of Würzburg, 97074 Würzburg — ²ZAE Bayern, 97074 Würzburg — ³University of Santa Barbara, Santa Barbara, CA 93106, USA

In donor-acceptor based bulk-heterojunction solar cells, the splitting

of singlet excitons at the donor and acceptor interface is of crucial importance for charge generation. The reversed process, in which two initially free charge carriers meet at the interface to form an exciton with singlet or triplet multiplicity is rather beneficial for light emission in OLEDs but considered as one of the loss factors in OPV.

In our experiments, the occurrence of triplet excitons and CT states was probed by using spin sensitive detection of the photo- and electroluminescence. A substantial generation of molecular triplet excitons was found in high efficiency donor-acceptor OPV systems based on the low bandgap copolymer PTB7 and in the soluble small molecule p-DTS(FBTTh2)2, both blended with PC70BM as acceptor. We ascribe these findings to an electron back transfer from the CT state to the triplet state on the donor material. In summary, the fundamental understanding of the transformation processes involving the CT states, triplet excitons, as well as free electrons and holes and their dependence on nanoscale morphology and energetics of blends is essential for the optimization of OPV devices.