

CPP 6: Charge Transfer Effects in Molecular Materials II (joint session CPP/HL/BP/DS)

Related to SYCT organized by Frank Schreiber (Tübingen) and Wolfgang Brütting (Augsburg).

Time: Monday 15:00–17:30

Location: H40

Invited Talk

CPP 6.1 Mon 15:00 H40
a molecular picture of charge-transfer processes at donor-acceptor interfaces in organic solar cells — ●JEAN-LUC BREDAS — School of Chemistry and Biochemistry/Center for Organic Photonics and Electronics, Georgia Institute of Technology, Atlanta, Georgia 30332-0400

Our objective in this presentation is two-fold. First, after a general introduction to organic solar cells, we use a molecular mechanics / molecular dynamics simulations approach to try and provide a molecular picture of the packing configurations (local morphology) at the interface between the donor and acceptor components in organic solar cells [1-3]. Then, we discuss in detail the impact that these local packing configurations at the interfaces have on the exciton-dissociation and charge-separation processes [4]. Systems under consideration include fullerene derivatives or n-type oligoacene derivatives as acceptors and low optical-gap polymers or small molecules (pentacene or squaraine derivatives) as donors.

References (1) N. Cates Miller, E. Cho, et al., *Advanced Materials*, in press (DOI: 10.1002/adma.201202293). (2) N. Cates Miller, E. Cho, et al., *Advanced Energy Materials*, in press (DOI: 10.1002/aenm.201200392). (3) Y.T. Fu, C. Risko, and J.L. Bredas, *Advanced Materials*, in press (DOI: 10.1002/adma.201203412). (4) J.L. Bredas, J. Norton, J. Cornil, and V. Coropceanu, *Accounts of Chemical Research* 42, 1691 (2009).

CPP 6.2 Mon 15:30 H40

Microscopic simulations of charge transport in disordered organic semiconductors — ●DENIS ANDRIENKO, BJOERN BAUMEIER, PASCAL KORDT, ANTON MELNYK, and CARL POELKING — Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany

Charge carrier dynamics in an organic semiconductor can often be described in terms of charge hopping between localized states. The hopping rates depend on electronic coupling elements, reorganization energies, and driving forces, which vary as a function of position and orientation of the molecules. The exact evaluation of these contributions in a molecular assembly is computationally prohibitive. Various, often semi-empirical, approximations are employed instead. Here, we review the current status of methods used to evaluate energetic disorder in organic semiconductors, such as polarizable force-fields and QM/MM approaches, focusing on their predictive power and accuracy. All methods are illustrated on donor-acceptor small-molecule interfaces as well as crystalline mesophases of conjugated polymers.

CPP 6.3 Mon 15:45 H40

Metal-Molecule Charge Transfer through Surface-Induced Conjugation — ●GEORG HEIMEL¹, STEFFEN DUHM², INGO SALZMANN¹, ALEXANDER GERLACH³, ANTIJE VOLLMER⁴, FRANK SCHREIBER³, and NORBERT KOCH¹ — ¹Institut für Physik, Humboldt-Universität zu Berlin, 12489 Berlin, Germany — ²Institute of Functional Nano & Soft Materials, Soochow University, Suzhou 215123, P. R. China — ³Institut für Angewandte Physik, Universität Tübingen, 72076 Tübingen, Germany — ⁴Helmholtz Zentrum Berlin für Materialien und Energie GmbH, 12489 Berlin, Germany

For the majority of large π -conjugated molecules, the Fermi level of supporting coinage-metal substrates is *pinned* to stay well within their electronic energy gap. In some cases, however, the Fermi level *does* cross into either of the frontier molecular orbitals. On the basis of a combined multi-technique experimental and theoretical study on a particularly clear-cut case – pentacenequinone and pentacenetetrone on the (111) surfaces of Au, Ag, and Cu – we present an attempt for a unifying explanation of such intriguing cases: The conjugation length of the organic semiconductor increases through interaction of specific chemical substituents with the metal surfaces. The ensuing reduction of the energy gap is found to be *the* crucial ingredient needed to overcome Fermi-level pinning. Our findings aid in the design of charged molecular monolayers, which are of interest both from the fundamental- and the applied-physics point of view.

Invited Talk

CPP 6.4 Mon 16:00 H40

High efficiency OLEDs based on delayed fluorescence — ●CHIHAYA ADACHI — OPERA, Kyushu University, Fukuoka, Japan

We achieved a novel pathway to reach the ultimate EL efficiency by inventing simple aromatic compounds displaying efficient thermally-activated delayed fluorescence (TADF) with high photoluminescence efficiency, namely *hyperfluorescence*. While we had previously assumed that the S1 level should be significantly higher than the T1 level, i.e., 0.5–1.0 eV higher, due to the presence of electron exchange energy, we found that the proper design of organic molecules can lead to a small energy gap (Δ EST) between them. Relatedly, a molecule displaying efficient TADF requires a very small Δ EST between its S1 and T1 excited states, resulting in enhanced T1 * S1 reverse intersystem crossing (ISC). Such excited states are attainable by the intramolecular charge transfer (CT) of a spatially separated donor and acceptor system. The critical point of the molecular design is the compatibility of a small Δ EST \sim 0 eV and a reasonable radiative decay rate of over 10⁶/s that overcomes competitive non-radiative decay paths, leading to highly luminescent TADF materials. Since the two properties conflict with each other, a delicate balance of the overlap of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) is required. Furthermore, to enhance the PL efficiency of a TADF material, geometrical change between its S0 and S1 states should be restrained to suppress non-radiative decay processes. In this work, we designed a novel series of highly efficient TADF emitters that resulted in very high electroluminescence efficiency.

CPP 6.5 Mon 16:30 H40

Triplet Exciton Generation and Electron Back Transfer in Organic Solar Cells — ●ANDREAS SPERLICH¹, HANNES KRAUS¹, STEFAN VÄTH¹, ALEXANDER FÖRTIG¹, CARSTEN DEIBEL¹, and VLADIMIR DYAKONOV^{1,2} — ¹Experimental Physics VI, Julius Maximilian University of Würzburg, 97074 Würzburg — ²ZAE Bayern, 97074 Würzburg

To increase the power conversion efficiency of organic solar cells it would be extremely advantageous to improve the harvesting of singlet and charge transfer (CT) excitons. Dissociation of CT complexes into free charge carriers or, alternatively, their decay by electron back transfer (EBT) reactions depend on the energy levels of constituting donor and acceptor molecules, on microscopic structure of blends but also on the relative spin orientation of charges carriers within the e-h pair. We report on state-of-the-art organic semiconductors for polymer-fullerene bulk hetero-junction solar cells, such as blends based on the benzodithiophene donor PTB7 or the endohedral fullerene-derivative Lu₃N@C₈₀-PCBEH. We applied optical, current-voltage, morphology, and spin-sensitive techniques and found correlations between electrical performance of solar cells and formation of CT and triplet states. Combining results of these complementary experiments, we offer a physical picture on how pushing up the LUMO level of acceptors or tailoring the blends' morphology may end up in unwanted loss mechanisms in bulk-heterojunction solar cells.

CPP 6.6 Mon 16:45 H40

Reduced recombination and field independent charge carrier generation in polymer-polymer solar cells — ●STEFFEN ROLAND¹, MARCEL SCHUBERT¹, ZHIHUA CHEN², ANTONIO FACCHETTI², and DIETER NEHER¹ — ¹University of Potsdam, Institute of Physics and Astronomy — ²Polyera Corporation

Charge transport and recombination are investigated for solar cells made of poly(3-hexylthiophene) (P3HT) and the non-fullerene, high mobility acceptor copolymer P(NDI2OD-T2). Optimized devices show high fill factors of up to 70%, indicating that the excellent electron transport properties of pure P(NDI2OD-T2) is prevailed in the blend. By applying of the time delayed collection field technique (TDCF) we measured the field dependence of the charge carrier generation, and of the non geminate recombination as well as the electron and hole mobilities. The results reveal a field-independent photocurrent generation and a strongly reduced recombination coefficient for free charge carriers. The results imply that major charge carrier losses originate from an ultrafast (geminate) recombination on time scales below 10 ns.

Invited Talk

CPP 6.7 Mon 17:00 H40

The role of intermolecular hybridization in molecular electrical doping — •INGO SALZMANN¹, GEORG HEIMEL¹, HENRY MÉNDEZ¹, ANDREAS OPITZ¹, PATRICK BARKOWSKI¹, MARTIN OEHZELT^{2,1}, KATREIN SAUER¹, and NORBERT KOCH^{1,2} — ¹Humboldt Universität zu Berlin — ²Helmholtz Zentrum Berlin, Germany

Molecular electrical doping of functional organic semiconductor (OSC) films is typically done by the admixture of strong molecular donors/acceptors as dopants. In a recent combined experimental and theoretical study on prototypical OSC/dopant pairs we showed that positive polarons, evidencing the common perception of direct electron transfer between the highest occupied molecular orbital (HOMO) of the OSC and the lowest unoccupied molecular orbital (LUMO) of the

p-dopant, are not observed in ultraviolet photoelectron spectroscopy even at considerable dopant ratios [1]. Instead of mutual ionization leading to singly occupied states, frontier molecular orbital hybridization between the OSC-HOMO and the dopant-LUMO occurs forming a *doubly occupied* bonding and an *empty* anti-bonding supramolecular hybrid orbital with a reduced fundamental gap, which is tunable by the acceptor strength. As all available states are occupied following Fermi-Dirac statistics, only a fraction of the hybrids is ionized at room temperature rationalizing the high dopant concentrations in practical applications. From this model, controlling the degree of hybridization emerges as strategy for the design of future improved molecular dopants in organic electronic devices.

[1] I. Salzmann, G. HeimeI et al., *Phys. Rev. Lett.* 108, 035502, 2012.