

CPP 9: Organic Electronics and Photovoltaics II: Doping (joint session CPP/DS/HL, organized by CPP)

Time: Monday 15:00–18:15

Location: ZEU 260

Invited Talk CPP 9.1 Mon 15:00 ZEU 260

Molecular Electrical Doping of Organic Semiconductors — ●INGO SALZMANN — Humboldt Universität zu Berlin, Berlin, Germany

In contrast to inorganic semiconductors, the potential of doping organic semiconductors (OSCs) for enabling new functionality and improving opto-electronic device performance has only recently been established. Here, the broad range of phenomena observed upon molecularly doping conjugated polymers (CPs) and molecules (COMs) is discussed, from which, finally, two different competing scenarios emerge [1]: (i) the formation of both OSC and dopant ions through integer-charge transfer, i.e., an ion pair (IPA), and (ii), the emergence of OSC/dopant ground-state charge transfer complexes (CPXs). In particular, the doping of poly(3-hexylthiophene) (P3HT) will be juxtaposed with that of quaterthiophene (4T) where, for both systems, an increase in thin-film conductivity by several orders of magnitude is observed. The underlying doping mechanisms at work are, however, fundamentally different [2]: IPA formation occurs for the polymer while CPX formation is found for the chemically and structurally similar oligomer. For both cases (i) and (ii), the doping-induced modification of the OSC density of states (DOS) is generally discussed for both p- and n-doping and its Fermi-Dirac occupation is modelled by numerical simulations. Therefrom finally emerges that engineering the DOS of doped OSCs, the occupation of which ultimately determines the doping efficiency, represents a key challenge in dopant design.

[1] I. Salzmänn et al., *Acc. Chem. Res.* 49, 370 (2016)

[2] H. Méndez et al., *Nature Commun.* 6, 8560 (2015)

CPP 9.2 Mon 15:30 ZEU 260

Inter-facial charge transfer studied in organic heterostructure field-effect transistors. — ●EDUARD MEISTER, STEFAN SCHMIDT, and WOLFGANG BRÜTTING — Institut für Physik, Universität Augsburg, Germany

In this work we studied inter-facial morphology dependent charge transfer (CT) happening in hetero-structure FETs based on vapour deposited small molecules. Therefore we used alpha-sexithiophene (α -6T) as donor and hexafluorotetracyanonaphthoquinodimethane (F₆TCNNQ) as acceptor. The lowest unoccupied molecular orbital of F₆TCNNQ is placed below of the highest occupied molecular orbital of α -6T, so that from an energetic point of view CT from α -6T to F₆TCNNQ molecules should occur. As evidence of CT we observed strong reduction of the switch-on voltage.

In order to get more information about morphology dependent CT and charge transport we produced devices with different gate insulator surfaces acting as template: blank SiO₂, as well as additional PMMA and thermally smoothed tetratetracontane [1] passivation layers. The morphology of α -6T layers was studied by atomic force microscopy and X-ray diffraction measurements. We employed also morphology dependent contact doping by application of tetrathiafulvalene tetracyanoquinodimethane salt contacts in contrast to mostly used gold electrodes. For the study of the transport mechanisms we performed temperature dependent measurements and calculated an upper limit of the activation energy for all the used configurations.

[1] L. Pithan et al., *J. Chem. Phys.* 143 (2015) 164707.

CPP 9.3 Mon 15:45 ZEU 260

Frontier orbital energy levels and exciton binding energies in organic charge transfer complexes — ●PAUL BEYER¹, STEFAN KRAUSE², TIMO FLORIAN¹, EDUARD MEISTER³, LUTZ GRUBERT⁴, WOLFGANG BRÜTTING³, NORBERT KOCH^{1,2}, and ANDREAS OPITZ¹ — ¹Dep. of Physics, Humboldt-Universität zu Berlin — ²Helmholtz-Zentrum Berlin — ³Institute of Physics, University of Augsburg — ⁴Dep. of Chemistry, Humboldt-Universität zu Berlin

The frontier π -orbitals of planar molecules tend to overlap upon contact and hybridization takes place resulting in charge transfer complexes (CTC) with modified energy levels [1]. We characterize the energy levels for the materials diindenoperylene (DIP) and hexafluorotetracyanonaphthoquinodimethane (F₆TCNNQ) in solution by cyclic voltammetry as well as in thin films and in planar heterojunction geometry by photoelectron spectroscopy. Optical transitions were measured by UV/Vis/NIR absorption and X-ray transitions by

near edge X-ray absorption fine structure spectroscopy.

At the planar DIP/F₆TCNNQ interface CTC formation occurs. Due to the energy level alignment at the interface, which will be shown in detail for standing and lying molecular orientations, and the lower gap of the CTC in contrast to the semiconductor DIP, doping is present and DIP field-effect transistors with F₆TCNNQ deposited on top are showing a strongly reduced threshold voltage. Furthermore, the exciton binding energies, which are much larger for X-ray than for optical excitations, will be discussed together with the energy levels.

[1] H. Méndez et al., *Nat. Commun.* 6 (2015) 8560.

CPP 9.4 Mon 16:00 ZEU 260

Conical Intersection Dynamics of F4TCNQ Anion Radical doped Conducting Polymer Observed by 2D Electronic Spectroscopy — AJAY JHA¹, HONG-GUANG DUAN^{1,2,3}, ●VANDANA TIWARI¹, MICHAEL THORWART^{2,3}, and R. J. DWAYNE MILLER^{1,3,4} — ¹MPI-Structure & Dynamics of Matter, Hamburg, Germany — ²Universität Hamburg, Germany — ³CUI Hamburg, Germany — ⁴University of Toronto, Canada

Quinones are well celebrated electron acceptors which are even employed by nature for their impressive ability to retain electrons e.g. ubiquinone and plastoquinone. Quinone derivatives like tetrafluoro-tetracyano-quinodimethane (F4TCNQ) are popularly used as a p-type dopant to obtain high conducting polymer blend. To achieve higher conductivity, there has been a constant empirical effort to obtain different derivatives of quinones. In order to develop a molecular basis for rational tailoring F4TCNQ unit, understanding the electronic structure and relaxation dynamics of the TCNQ doped within a polymer framework is paramount. We have employed two-dimensional electronic spectroscopy to probe the coherent dynamics of F4TCNQ with the semiconducting polymer forming a charge transfer complex. We captured an ultrafast decay of F4TCNQ- mediated by conical intersection which is in agreement with the photoelectron spectroscopic studies in gas-phase. Additionally, we also observe that electronic transitions in F4TCNQ- are strongly coupled to polymer cation electronic structure. Our results open up new perspectives for tailoring intermolecular interactions to obtain high electrical conductivities.

CPP 9.5 Mon 16:15 ZEU 260

Electronic structure of charge transfer compounds using Fermi-Löwdin orbital self-interaction corrected DFT — ●TORSTEN HAHN¹, MARTIN KNUPFER², and FLORIAN RÜCKERL² — ¹Institute for Theoretical Physics, TU Freiberg, Freiberg, Germany — ²Institute for Solid State Research, IFW Dresden, Germany

We present experimental and theoretical results on novel Picene/F4TCNQ and related donor / acceptor systems [1,2]. The recently developed Fermi-Löwdin orbital based approach for self-interaction corrected density functional theory (FLO-SIC DFT [3,4]) is used to investigate the electronic structure of these materials. The theoretical results are compared to standard DFT calculations and experimental data obtained by photoemission spectroscopy. We focus our analysis on the description of the magnitude of the ground state charge transfer and on the details of the formed hybrid orbitals. Further, we show that for weakly bound donor / acceptor systems the FLO-SIC approach delivers a more realistic description of the electronic structure compared to standard DFT approaches.

[1] B. Mahns, et al., *Cryst. Growth Des.* 14, 1338 (2014).

[2] F. Ruckerl et al., *JCP* 145, (2016).

[3] M. R. Pederson et al., *JCP* 140, 121103 (2014).

[4] M. R. Pederson, *JCP* 142, 064112 (2015).

15 min break

CPP 9.6 Mon 16:45 ZEU 260

UV-Vis-NIR spectroscopy studies on molecularly doped semiconducting polymers — ●MALAVIKA ARVIND¹, PATRICK PINGEL², SILVIA JANIETZ², and DIETER NEHER¹ — ¹University of Potsdam, Soft Matter Physics, Germany — ²Fraunhofer Institute for Applied Polymer Research, Potsdam, Germany

In recent years, significant efforts have been devoted towards under-

standing the fundamental processes involved in the doping of organic semiconductors with small molecules. Nevertheless, there is still a large degree of ambiguity in the field, which has prevented us from being able to truly exploit this method to better our organic devices. In this work, we utilize UV-Vis-NIR spectroscopy to study the sub-band gap optical transitions that occur in the well known semiconducting polymer poly(3-hexylthiophene) (P3HT) when doped with tris(pentafluorophenyl)borane (BCF), a strong Lewis acid, and compare it to the more commonly studied p-dopant, tetrafluorotetracyanoquinodimethane (F4TCNQ). In spite of the dissimilarity in their structures, both dopants are found to efficiently create positive polarons in P3HT, in solutions as well as in films. Here we investigate the influence of various parameters such as polymer/dopant concentration, solvent, temperature on the nature and efficiency of molecular doping, and also address the question of whether pre-aggregation of the polymer in solution assists or suppresses polaron-formation in P3HT.

CPP 9.7 Mon 17:00 ZEU 260

Redox-Potentials Outperform Ionization Energy / Electron Affinity for Predicting Ion Pair Formation in Molecular Electrical Doping — ●BERTHOLD WEGNER¹, LUTZ GRUBERT², DENNIS CHERCKA³, ANDREAS OPITZ⁴, STEFAN HECHT², KLAUS MÜLLEN³, and NORBERT KOCH^{1,4} — ¹Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Berlin, Germany — ²Institut für Chemie, Humboldt-Universität zu Berlin, Berlin, Germany — ³Max-Planck-Institut für Polymerforschung, Mainz, Germany — ⁴Institut für Physik & IRIS Adlershof, Humboldt-Universität zu Berlin, Berlin, Germany

Electrical doping with strong molecular donors and acceptors is a key technological component to control the charge carrier density and Fermi level of organic semiconductors. While commonly ionization energy / electron affinity values (measured on thin films via ultraviolet / inverse photoelectron spectroscopy) are employed to guide the selection of molecular dopants for organic hosts, we find strong indications that redox-potentials (measured in solution via cyclic voltammetry) are indeed better suited. A set of donor-acceptor systems, both in solution and in thin films, is studied using structurally similar molecules. Our results show that redox-potentials provide a useful basis to predict ion pair formation in the studied systems, while ionization energies / electron affinities fail to provide such a basis. This is ascribed to the molecular length scale dopant-host interaction well described by local redox events at the molecule-electrode interface, whereas thin film ionization and affinity level measurements include collective and long-range solid state properties.

CPP 9.8 Mon 17:15 ZEU 260

Effective work function reduction of practical electrodes using an organometallic dimer — KOUKI AKAIKE¹, MARCO V. NARDI¹, MARTIN OEHZELT^{2,1}, JOHANNES FRISCH^{2,1}, ●ANDREAS OPITZ¹, CHRISTOS CHRISTODOULOU¹, GIOVANNI LIGORIO¹, PAUL BEYER¹, MELANIE TIMPEL¹, IGOR PIS³, FEDERICA BONDINO⁴, KARTTIKAY MOUDGIL⁵, STEPHEN BARLOW⁵, SETH R. MARDER⁵, and NORBERT KOCH^{1,2} — ¹Humboldt-Universität zu Berlin, Germany — ²Helmholtz-Zentrum Berlin, Germany — ³Elettra-Sincrotrone Trieste, Italy — ⁴IOM CNR Laboratorio TASC, Italy — ⁵Georgia Institute of Technology, USA

The control of the cathode work function (WF) is essential to enable efficient electron injection and extraction at organic semiconductor/cathode interfaces in organic electronic devices. Here, ultraviolet photoelectron spectroscopy is used to determine the work function reduction by moderately air-stable pentamethylrhodocene dimer onto various conducting electrodes, by either vacuum deposition or drop casting from solution, to less than 3.6 eV, with 2.7 eV being the lowest attainable value. Electron transfer from the molecule to the respective substrates is responsible for the appreciable WF reduction. Notably, even after air exposure, the WF of the donor-covered electrodes remains below those of typically used clean cathode metals, such as Al and Ag. This demonstrates the ability of the pentamethylrhodocene dimer to reduce the WF for a wide range of electrodes used in all-organic or organic-inorganic hybrid devices.

K. Akaike et al., *Adv. Funct. Mater.* **26** (2016) 2493-2502.

CPP 9.9 Mon 17:30 ZEU 260

Temperature-induced F4TCNQ desorption from p-doped P3HT films — ●HANNES HASE¹, ANDREAS OPITZ¹, NORBERT KOCH^{1,2,3}, and INGO SALZMANN¹ — ¹Humboldt-Universität zu Berlin,

Supramolekulare Systeme, Germany — ²Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Bereich Solarenergieforschung, Germany — ³Jiangsu Key Laboratory for Carbon-Based Functional Materials & Devices, Institute of Functional Nano & Soft Materials (FUNSOM), Soochow University, Suzhou 215123, P.R. China

Thermal post-fabrication annealing is common practice for functional conjugated polymer (CP) films in organic photovoltaic cells, which is also applied to p-doped CPs in a number of studies. However, the typically small molecular-weight dopants, like, e.g., tetrafluorotetracyanoquinodimethane (F4TCNQ), can be expected to be prone to diffusion upon thermal treatment, which has been largely disregarded in pertinent literature. Here, we explore to which extent the annealing temperature impacts films of poly(3-hexylthiophene-2,5-diyl) (P3HT) doped with F4TCNQ. For temperatures beyond 60 °C, we find a reduction in conductivity with a concomitantly lowered dopant concentration, as deduced from optical and Fourier-transform infrared spectroscopy. While atomic force microscopy indicates the morphology to be essentially retained, grazing-incidence X-ray diffraction confirms the transition from a P3HT/F4TCNQ mixed crystal structure to pure P3HT and points towards F4TCNQ desorption. We conclude that, upon thermal annealing, dopant loss needs to be accounted for by adjusting the dopant concentration.

CPP 9.10 Mon 17:45 ZEU 260

Molecular drift of p-type dopants in doped organic semiconductors driven by an external electric field and studied by spectroscopic IR-microscopy — ●SEBASTIAN BECK^{1,2}, VIPI-LAN SIVANESAN^{1,2}, LARS MÜLLER^{2,3}, SEON-YOUNG RHIM^{1,2}, JAKOB BERNHARDT^{1,2}, and ANNEMARIE PUCCI^{1,2} — ¹Universität Heidelberg, Kirchhoff-Institut für Physik — ²InnovationLab GmbH, Heidelberg — ³TU Braunschweig, Institut für Hochfrequenztechnik

A homogeneous dopant distribution is known to be important for efficient charge transfer (CT) in doped organic semiconductors as well as the functionality of organic electronic devices. Therefore, a lot of effort is made to control the molecular composition in devices throughout the deposition process. However, during device operation an unintentional movement of charged molecules such as dopants through the layers can occur and can reduce or even destroy device performance. To further improve the understanding of these effects the implementation of new analytical methods is advised. In this study, the motion of the p-type dopant Mo(tfdCO₂Me)₃ in highly regioregular P3HT induced by an external electric field was studied with spectroscopic IR-microscopy. The molecular drift was identified by measuring laterally resolved IR spectra of doped layers between two electrodes before and after applying a dc field of about 2 V/micron. An analysis of the changes of the vibrational modes of the dopant molecule as well as the spectral features of the charged P3HT chains enabled an estimate of the mobility of the dopant molecules. Our results are in agreement with electrical measurements and clarify underlying processes of device fatigue.

CPP 9.11 Mon 18:00 ZEU 260

Drift of Dopants in Organic Semiconductors — ●LARS MUELLER^{1,2,3}, SEON-YOUNG RHIM^{1,3}, VIPI-LAN SIVANESAN^{1,3}, DONGXIANG WANG¹, SEBASTIAN BECK^{1,3}, ANNEMARIE PUCCI^{1,3}, WOLFGANG KOWALSKY^{1,2,3}, and ROBERT LOVRINCIC^{1,2} — ¹InnovationLab, Heidelberg, Germany — ²Institute for High-Frequency Technology, TU Braunschweig, Germany — ³Kirchhoff Institute for Physics, Heidelberg University, Germany

Electrical doping of organic semiconductors is widely applied to fabricate high performance organic electronic devices. The usually unwanted but still prevalent effect of dopant mobility in organic semiconductors is known for various dopant molecules in terms of diffusion towards a stable equilibrium. A mostly neglected effect is the influence of operating conditions that can cause a drift of dopants additionally to the known diffusion. We study this drift behavior and compare different dopant-host combinations, starting from Poly(3-hexylthiophen-2,5-diyl) (P3HT) doped with 2,3,5,6-Tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4TCNQ) to larger dopant molecules and different host materials. We find a dynamic drift-process that can be utilized to deliberately create highly doped and almost undoped regions within one thin film, resulting in a spatially altered conductivity. To demonstrate the applicability, we show first data of a proof-of-principle memory device that is based on a spatially controlled dopant distribution.