

CPP 77: Organic Electronics and Photovoltaics - Transport and Doping

Time: Friday 9:30–13:00

Location: C 243

Invited Talk

CPP 77.1 Fri 9:30 C 243

High-Performance Organic Transistors — ●KARL LEO — IAPP, TU Dresden, 01062 Dresden

Organic field effect transistors (OFET) have so far not achieved major commercial impact, despite their many attractive properties such as low-cost, low-temperature processing, and flexibility. In this talk, I will discuss recent work which addresses some of the shortcomings of the OFET. One key approach is to introduce controlled electrical doping into OFET structures /1/. We have recently shown /2,3/ that this allows for the first time the realization of organic inversion transistors. Furthermore, I will discuss vertical transistor structures which have very short channel length without micropatterning. These structures allow much higher current densities than the lateral OFET despite rather simple processing technology without high-resolution patterning /4,5/. These devices are well suited to drive organic light emitting diodes (OLED), allowing all-organic flexible OLED displays. Recently, we have achieved current densities as high as kA/cm² and frequencies above 30MHz /6/.

/1/ K. Walzer et al., Chem. Rev. 107, 1233 (2007) /2/ B. Lüssem et al., Nature Comm. 4, 2775 (2013) /3/ A.A. Guenther et al., APL 106, 233301 (2015) /4/ A. Fischer et al., Appl. Phys. Lett. 101, 213303 (2012) /5/ M.P. Klinger et al., Adv. Mat. 27, 7734 (2015) /6/ M. P. Klinger et al., Nat. Sci. Rep. 7, 4471 (2017)

CPP 77.2 Fri 10:00 C 243

How does molecular structure influence charge mobility? - Mining a database of organic semiconductors. —

●CHRISTIAN KUNKEL, CHRISTOPH SCHOBER, JOHANNES MARGRAF, KARSTEN REUTER, and HARALD OBERHOFER — Technische Universität München

Improving charge carrier mobilities in organic semiconductors is a challenging task, usually tackled by structural tuning of a promising compound family, while relying on intuition or experience. Still, the vast chemical space is then only locally explored, while promising design strategies might also be uncovered from systematic analysis of large compound databases. We carry out such an analysis by applying charge carrier mobility simulations and data mining strategies to an inhouse database of > 64.000 organic crystals, obtained from the Cambridge Structural Database (CSD) and screened for charge transport properties using first principle derived descriptors. The analysis shows, that our screening recovers many known and well performing materials, while also finding many promising candidates, not yet considered for organic electronics applications. To further derive design principles from the data, we evaluate the intrinsic suitability of ≈ 200 molecular scaffolds found to be contained as compound-clusters in our database. A similarity network analysis hints at already explored regions of chemical space, while statistical analysis of the clusters uncovers significant expectable performance differences. Such information can be the basis for further in-depth theoretical and experimental design of materials for organic electronics, highlighting the value of data-based approaches.

CPP 77.3 Fri 10:15 C 243

Charge transport of thiophene containing D/A small conjugated molecules and monomer in π - π isolated stacks — ●DEYAN RAYCHEV^{1,2}, GOTTHARD SEIFERT^{1,3}, JENS-UWE SOMMER^{1,2,4}, and OLGA GUSKOVA^{1,2} — ¹DCMS, TU Dresden — ²Leibniz IPF Dresden — ³Theoretical Chemistry, TU Dresden — ⁴Institute for Theoretical Physics, TU Dresden

A lot of effort has been done in order to improve the performance of organic electronics devices. Since the charge transport (CT) in technology relevant materials is a multiparametric problem, it is very challenging task to predict these properties in computer simulations. Here, we investigate CT properties of benzothiadiazole (BTZ) and diketopyrrolopyrrole (DPP) based molecules linked with thiophene (Th) as a flanking unit and their monomer (Th-BTZ-Th, Th-DPP-Th and Th-BTZ-Th-DPP-Th) in segregated and mixed π - π stacks using DFT and semiclassical Marcus theory. Scanning the potential surface of the molecules in stacks, we found out that the configurations with minimal binding energies are very close to the experimental crystal structures. For such mixed π - π isolated stacks, the hopping mobilities are calculated and compared with experimental data. Interestingly, the predicted values are very close to the measured mobilities for polymer

[1] and molecular crystals [2, 3].

This work is supported by ERDF and Free State of Saxony via ESF project 100231947. [1] P. Sonar et. al., Adv. Mater., 2010, 22, 5409-5413. [2] P. B. Pati et. al., ACS Appl. Mater. Interfaces, 2013, 5, 12460-12468. [3] J. Dhar et. al., Chem. Commun., 2015, 51, 97-100.

CPP 77.4 Fri 10:30 C 243

Measuring the Lateral Charge-Carrier Mobility in Metal-Insulator-Semiconductor Capacitors via Kelvin-Probe —●KARL-PHILIPP STRUNK¹, VALERIA MILOTTI¹, ALEXANDER ULLRICH², and CHRISTIAN MELZER¹ — ¹Centre for Advanced Materials, University of Heidelberg, Germany — ²Organisch-Chemisches Institut, University of Heidelberg, Germany

DC current-voltage measurements on organic field-effect transistors are commonly used to characterize the planar electrical transport in organic semiconductors. We have reported an alternative AC dark-injection method giving access to in-plane transport parameters of organic semiconductor thin films. Exposing a metal-insulator-semiconductor structure to a periodic bias leads to a periodic change in surface potential which can be tracked via a Kelvin-Probe giving direct insight into the movement of lateral charge-carrier waves along the organic film. Based on a simple model the charge-carrier mobility of the semiconducting layer can be extracted from experimental data. In this study we further investigate the validity of the proposed model via two dimensional finite-element simulations. We investigate the influence of properties like doping concentration, traps states and applied bias on the device response. It is found that the model predicts the surface potential oscillations very well for a wide range of parameters. Ad-hoc expansions of the model to include additional effects such as doping and traps states further increase its accuracy, giving it a broad applicability if accurate experimental measurements of the mobility are needed.

CPP 77.5 Fri 10:45 C 243

Studying the Mobility of Metal-Organic Frameworks —

●CHRISTOPH MUSCHIELOK and HARALD OBERHOFER — Technische Universität München, Germany

Metal-Organic Frameworks (MOFs) are artificial, self-assembled networks of metal centers connected by organic linker molecules. They exhibit large pores, into which small molecules may be absorbed. This structural feature can be exploited in a hypothetical MOF-based trace gas surface acoustic wave (SAW) sensor. Such a device needs – from a theorist’s point of view – a profound knowledge of the charge carrier mobility and density within MOFs.

Contrary to most MOFs the class of metal triazolates, notably iron-(II)-triazolate, have quite recently been found to show promising conductive properties. It is now crucial to understand why in particular these compounds have such a high mobility compared to other MOFs. Therefore, we study the applicability of different charge transport (CT) models to the mobility of the charge carriers in metal triazolates based mainly on density-functional theory (DFT).

Starting from there, we also focus on the development of general design principles for semiconducting MOF materials. These can provide guidelines for MOF synthesis to ultimately enable the tailoring of MOF properties to a variety of specific use-cases.

15 min. break

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Band bending in crystalline silicon induced by molecular doped P3HT —

●MATTHIAS ZELLMEIER, MATHIAS MEWS, DOROTHEE MENZEL, LARS KORTE, and JÖRG RAPPICH — Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Institut für Silizium-Photovoltaik, Kekuléstr. 5, 12489 Berlin, Germany

Molecular doping of the organic semiconductor poly-(3-hexylthiophene), P3HT, with the strong molecular acceptor 2,3,5,6-tetrafluorotetracyano-quinodimethane, F4TCNQ, is one of the most common techniques to overcome the restriction of low conductivity in this organic material. The well-established method leads to a decrease of the hole mobility in the low-to-medium doping regime, while the hole density increases linearly with the doping concentration. Additionally, it presents an important prerequisite towards controlling p/n-junctions

involving organic materials. Hybrid interfaces combining organic materials and inorganic semiconductors are of special importance as they are crucial for the performance of most applications, e.g. light emitting devices or solar cells. Employing photoelectron spectroscopy, we studied the interface between crystalline silicon, c-Si, and doped P3HT. The doping in the spin coated organic layer was varied from a low doping concentration of 1:1000 F4TCNQ molecules per 3HT monomer units up to 1:3. UPS was used to monitor the development of the HOMO-onset upon doping as well as the work function. A special focus is placed on the shift of the silicon 2p orbital binding energy, which is measured using XPS. The data is used to extract the band bending at the silicon/organic semiconductor junction.

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Doping of Semiconducting Polymers: Structural Order and Dopant Drift — ●LARS MÜLLER^{1,2,3}, SEBASTIAN BECK^{1,3}, WEN-LAN LIU^{1,4}, ANNEMARIE PUCCI^{1,3}, ANDREAS KÖHN⁴, 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 — ⁴Institute for Theoretical Chemistry, University of Stuttgart, Germany

Electrical doping of organic semiconductors is widely applied to fabricate high performance organic electronic devices. First, this contribution studies the electric-field-induced drift of molecular dopants for different host-dopant combinations and the influence of structural order on this drift [1]. Second, we present a study that focuses on the spatial position of dopant molecules in P3HT crystallites, together with a DFT-based approach that can explain the observed changes in π - π lattice spacing without the need for a dopant intercalation. The drift study includes Poly(3-hexylthiophene-2,5-diyl) (P3HT) doped with 2,3,5,6-Tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4TCNQ), as well as larger dopant molecules and different host materials. We find that the dynamic drift-process can be utilized to deliberately create highly doped and almost undoped regions within one thin film, resulting in a spatially altered conductivity. The applicability is shown on proof-of-principle memristive devices that are based on this effect.

[1] L. Müller et al., *Adv. Mater.* 2017, 1701466.

CPP 77.8 Fri 11:45 C 243

Quantitative Molecular Doping and Electron Trapping in Single-Wall Carbon Nanotubes — ●MICHAEL AUTH¹, BERND STURDZA¹, KLAUS H. ECKSTEIN², FLORIAN OBERNDORFER², ANDREAS SPERLICH¹, TOBIAS HERTEL², and VLADIMIR DYAKONOV^{1,3} — ¹Experimental Physics VI, Julius Maximilian University of Würzburg, 97074 Würzburg — ²Institute of Physical and Theoretical Chemistry, Julius Maximilian University of Würzburg, 97074 Würzburg — ³Bayerisches Zentrum für Angewandte Energieforschung (ZAE Bayern), 97074 Würzburg

Defects and doping in Single-Wall Carbon Nanotubes (SWNTs) by (electro-) chemical methods is a highly important topic for future applications of SWNTs. Previous indirect all-optical techniques hypothesise charge carrier localisation in SWNTs due to adjacent AuCl₃ molecules, which is indicated by changing exciton dynamics¹. Here, we present direct quantitative investigations of chemical p-doping by means of electron paramagnetic resonance (EPR), using a spin count reference sample. We estimated the p-doping concentrations on our SWNTs over a wide range, gaining new insight into the widely discussed topic of charge carrier confinement.

1. Eckstein et. al., Localized Charges Control Exciton Energetics and Energy-Dissipation in Doped Carbon Nanotubes, *ACS Nano* 2017, DOI:10.1021/acsnano.7b05543

CPP 77.9 Fri 12:00 C 243

Direct evidence of strong detrimental electronic interactions in solution processed doped organic semiconductors — ●AJAY JHA¹, HONG-GUANG DUAN^{1,2,3}, VANDANA TIWARI¹, MICHAEL THORWART^{2,3}, and R. J. DWAYNE MILLER^{1,3,4} — ¹MPSD, Hamburg, Germany — ²I. Institut für Theoretische Physik, UH, Germany — ³CUI, Hamburg, Germany — ⁴University of Toronto, Canada

Understanding the inherent electronic structure the ion-pairs is essential to formulate a rational basis for charge mobilities in doped organic electronic circuits. Here we apply two-dimensional electronic spectroscopy to investigate the electronic dynamics of ion-pair in a solution of F4TCNQ-doped conducting polymer, PBTTT as a model system. The Coulombic interaction between cation and anion results in strong electronic coupling within the PBTTT+F4TCNQ- ion-pair which is

manifested by the well-resolved off-diagonal peaks in 2D spectra envisaging the electronic connectivity among the ions. A theoretical model which simulates the experimental data reveals that the electronic coupling strength of 250 cm⁻¹ with an intermolecular distance of 4.5 Å between the ions. Our experiments in combination with the theoretical modeling capture the molecular details of the ion-pair which should pave the way towards rational tailoring of the ion-pairs in solution.

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The density of states of n-doped organic thin films from simulations and experiments — CHRISTOPHER GAUL¹, SEBASTIAN HUTSCH¹, MARTIN SCHWARZE², SEBASTIAN SCHELLHAMMER¹, FABIO BUSSOLOTTI³, SATOSHI KERA³, GIANAURELIO CUNIBERTI¹, KARL LEO², and ●FRANK ORTMANN¹ — ¹Center for Advancing Electronics Dresden, TU Dresden, Germany — ²Dresden Integrated Center for Applied Physics and Photonic Materials, TU Dresden, Germany — ³Institute for Molecular Science, Okasaki, Japan

Doping plays a crucial role in semiconductor physics where n-doping is controlled by the ionisation energy of the impurity relative to the conduction band edge. In organic semiconductors, efficient doping may be dominated by different effects, which are presently not well understood. Here, we study n-doping of C60 as prototypical material by simulating the density of states of the doped system in the density functional theory framework. We simulate the Fermi level position which compares well with experimental results from direct and inverse photoemission spectroscopy. From these results, we extract relevant factors that influence the doping efficiency.

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State of matter dependent charge transfer interactions between planar molecules for doping applications — ●ANDREAS OPITZ¹, PAUL BEYER¹, DUC PHAM¹, CLEA PETER¹, NORBERT KOCH^{1,2}, DMITRII NABOK¹, CLAUDIA DRAXL¹, LUTZ GRUBERT¹, STEFAN HECHT¹, and CATERINA COCCHI¹ — ¹Humboldt-Universität zu Berlin, Germany — ²Helmholtz-Zentrum Berlin, Germany

Controlling the electrical conductivity of organic semiconductors is a key requirement for organic electronics, nowadays realized mostly by molecular dopants. Two doping mechanisms, i.e., charge transfer complex (CTC) and ion pair (IPA) formation, have been reported, but their occurrence depending on molecular structure, energy levels, and structure of thin films is elusive. Here, we study the p-type doping of the planar molecule dibenzo-tetrathiafulvalene (DBTTF) as semiconductor, with the planar electron acceptors tetracyano-naphthoquinodimethane (TCNNQ) and hexafluoro-TCNNQ (F6TCNNQ) as dopants. The conductivity increase is stronger for F6TCNNQ than for TCNNQ. Optical spectroscopy reveals the presence of CTCs for DBTTF:TCNNQ blends and CTC and IPA formation for DBTTF:F6TCNNQ blends. We discuss the different fundamental semiconductor-dopant interactions in solution and in solid-state with the aid of energy levels measurements, many-body perturbation theory calculations, absorption and vibrational spectroscopy. The presence of both charge transfer mechanisms in this set of compounds gives us access to their doping efficiency, which is higher for IPA than for CTC formation.

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Photoinduced Charge Carrier Transport at (001) Pentacene/Perfluoropentacene Crystal Interfaces — ●SEBASTIAN HAMMER¹ and JENS PFLAUM^{1,2} — ¹Experimental Physics VI, Julius Maximilian University of Würzburg, 97074 Würzburg — ²Bavarian Center for Applied Energy Research (ZAE Bayern), 97074 Würzburg

Mixed Pentacene:Perfluoropentacene (P:PFP) thin films have been reported archetypical donor-acceptor heterojunctions for examining the optical characteristics of charge transfer states [1]. However, aiming for possible effects on charge carrier transport at P/PFP interfaces, thin film boundaries impose severe limitations and thus, require the examination of photoinduced effects on the interface conductivity by means of well-defined crystal surfaces. For this purpose, pentacene single crystals were grown by horizontal physical vapor deposition with the (001) orientation of the crystal surface being confirmed by X-ray diffraction. PFP layers of various thicknesses between 5 to 50 nm were evaporated on top of the (001) surface and their morphology was analyzed by complementary AFM and XRD measurements. Illuminating the (001) P/PFP interface with a 532 nm cw-laser we observed a pronounced increase of the interface conductivity by up to 50% with respect to the neat pentacene crystal depending on the PFP top layer thickness as well as on the electric field applied. Utilizing different illumination geometries and temperature dependent measurements we

will discuss the origin of the conductivity increase and its relation to charge transfer states and injection effects.

[1] Anger, F., et. al., *JCP* **136**, 054701 (2012)