

HL 50: Organic semiconductors

Time: Wednesday 9:30–12:30

Location: H13

HL 50.1 Wed 9:30 H13

Strain derivatives for localized-orbital based electronic-structure theory and application to organic semiconductors

— ●FRANZ KNUTH, CHRISTIAN CARBOGNO, VOLKER BLUM, VIKTOR ATALLA, and MATTHIAS SCHEFFLER — Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany

The carrier levels of semiconductor materials can depend sensitively on strain and pressure. Here, we discuss the analytical implementation of strain derivatives, i.e. the stress tensor, for first-principles calculations in the density-functional framework based on numeric atom-centered orbitals in the all-electron FHI-aims code [1]. Besides the contributions for calculations with LDA/GGA functionals, we include the components needed for non-local hybrid functionals and van der Waals effects [2]. The last two elements are critical ingredients especially for the accurate description of the electronic structure of organic semiconductor materials, their band gaps and deformation potentials. We present benchmark results for various test systems, in particular for crystalline models of polyacetylene.

[1] V. Blum *et al.*, *Comp. Phys. Comm.* **180**, 2175 (2009).[2] A. Tkatchenko and M. Scheffler, *PRL* **102**, 073005 (2009).

HL 50.2 Wed 9:45 H13

Exploring molecular-scale structure formation of HIOS— ●KAROL PALCZYNSKI¹ and JOACHIM DZUBIELLA² — ¹Institut für Physik, Humboldt Universität zu Berlin, Newtonstr. 15, 12489 Berlin, Germany — ²Institut für Physik, Humboldt Universität zu Berlin, Newtonstr. 15, 12489 Berlin, Germany

The optical and electronic properties of Hybrid Inorganic/Organic Semiconductor (HIOS) devices strongly depend on the molecular configuration of the conjugated organic molecules at the inorganic semiconductor surfaces. The goal of this work is to explore the structure formation of para-Sexiphenyl (6P) on a molecular level by applying atomistically resolved molecular dynamics (MD) computer simulations. The temperature dependent crystal structure of 6P has been analyzed by means of orientational and conformational order parameters. The sensitivity of the obtained structures to atomic partial charges and charge distributions has been studied and the calculated results have been compared with experimental x-ray data.

HL 50.3 Wed 10:00 H13

DFT study of vibronic properties of fluorinated nickel phthalocyanine — ●DAVOUD POULADSAZ — Max Planck Institute for the Physics of Complex Systems, Dresden, Germany

Due to their electronic, optical, and structural properties, metal-phthalocyanines, a class of organic semiconducting dye molecules, have attracted considerable attention for their wide range of application including chemical sensors and photovoltaic devices, for which fundamental understanding of charge transport properties of the molecules is crucial. In π -conjugated systems, the electronic transport properties are manipulated by the strong coupling between geometric and electronic structure. The electronic transport is efficient when the electronic coupling between adjacent molecules is maximized and the reorganization energy is minimized. On the other hand, fluorinated phthalocyanines are shown to be sensitive to reducing gases due to the withdrawing effect of fluorine atoms. Therefore, by means of density functional theory, we have calculated the intramolecular reorganization energy and vibronic couplings for single fluorinated nickel phthalocyanine, which originate from the change in optimized geometry of the molecule due to the ionization. The results reveal how the reorganization energy and the vibronic couplings change due to the fluorination of the molecule.

HL 50.4 Wed 10:15 H13

Trap passivation in organic semiconductors using ultra-low molecular doping — ●SELINA OLTHOF^{1,2}, SWAGAT MOHAPATRA³,SANJEEV SINGH⁴, STEPHEN BARLOW³, SHAFIGH MEHRAEEN³, VEACESLAV COROPCEANU³, JEAN-LUC BRÉDAS³, SETH MARDER³, BERNARD KIPPELEN⁴, and ANTOINE KAHN² — ¹Institut für Physikalische Chemie, Universität zu Köln, Germany — ²Department of Electrical Engineering, Princeton University, USA — ³Center for Organic Photonics and Electronics and School of Chemistry and Bio-chemistry, Georgia Tech, Atlanta, USA — ⁴Center for Organic Photonics and Electronics and School of Electrical and Computer Engineering, Georgia Tech, Atlanta, USA

Trap states in the band gap of organic semiconductors play a detrimental role in the performance of devices. We use charge carriers released from ultra low amounts of a molecular n-dopant to gradually fill up and thereby passivate trap states in the matrix material C60. The changes in Fermi level position as well as charge carrier transport are investigated. Experiments and kinetic Monte Carlo simulations confirm a distinct change in electronic behavior for doping concentration below and above typical trap densities. After passivation, an increase in C60 electron mobility by more than three orders of magnitude is achieved. We show that in organic field effect transistors the device performance can be greatly improved by trap filling, with high current on/off ratios as long as the doping concentration is kept below the trap density of the matrix. Controlled ultra-low doping is shown to be an effective way to passivate unwanted traps in organic semiconductor films.

HL 50.5 Wed 10:30 H13

Polarization resolved carrier dynamics in crystalline perfluoropentacene films — ●KOLJA KOLATA, TOBIAS BREUER, GREGOR WITTE, and SANGAM CHATTERJEE — Philipps-Universität Marburg

Perfluoropentacene (PFP) is a promising n-type counterpart to the p-type pentacene (PEN) for possible future organic pn-junction applications. Since the synthesis of PFP only dates back to 2004 little is known about the electronic excitations and dynamics in this material system. We performed polarization resolved optical pump-probe spectroscopy on highly ordered, crystalline PFP-films epitaxially grown on NaF(100) in order to investigate its carrier dynamics. Due to the distinct crystal growth of PFP on NaF yielding single crystalline domains of $100 \mu\text{m}^2$ the optical response along the c- and b-axis can be probed independently. Two distinct time-regimes are observed in both crystal directions: an ultrafast decay ($\approx 1\text{ps}$) of the majority of the carriers followed by slower relaxation and recombination processes. Furthermore, a flat, broadband, induced absorption arises a few tens of femtoseconds after the excitation along the b-axis, where a pronounced π -stacking in the herringbone-structure exists. This induced absorption shifts towards higher energies during the following few tens of picoseconds indicating a relaxing carrier system. This confirms the different carrier dynamics and electronic properties along different directions within the PFP crystal.

Coffee break

HL 50.6 Wed 11:00 H13

The Effect of Confinement on the Exciton Dynamics in the Organic Semiconductor Rubrene — ●B. GIESEKING¹, T. SCHMEILER¹, B. MÜLLER¹, C. DEIBEL¹, V. DYAKONOV^{1,2}, and J. PFLAUM^{1,2} — ¹Experimental Physics VI, Julius-Maximilian University of Würzburg, D-97074 Würzburg — ²Bavarian Centre for Applied Energy Research (ZAE Bayern), D-97074 Würzburg

As for its inorganic counterpart the future developments in organic electronics are driven by the advancing device miniaturization. As a consequence the correlation between the opto-electronic properties and device dimensions has shifted continuously into the spotlight.

In this work we present a systematic investigation of the temperature dependent photoluminescence decay for well-defined structures of the organic semiconductor rubrene. The analysed samples exhibit an increasing degree of confinement and we confirm a direct influence on the PL spectra as well as on the excitation dynamics on ultrafast timescales already for a localization of excitation on the μm scale. Our results highlight the role of the local environment affecting the exciton dynamics in organic semiconductors which has to be taken into account for the design of future organic opto-electronic devices.

Financial support by the DFG (FOR 1809) is acknowledged.

HL 50.7 Wed 11:15 H13

Model-free mobility determination in thin films of organic semiconductors: potential mapping — ●JOHANNES WIDMER, JANINE FISCHER, KARL LEO, and MORITZ RIEDE — Institut für Angewandte Photophysik, TU Dresden, Germany

Mobility is the key parameter for charge transport characterization. In disordered systems, it is generally not a constant, but a function of the electric field and/or the charge carrier density.

In our work, we characterize the charge transport in thin films of organic semiconductors perpendicular to the surface, i.e. in the direction relevant for common device applications. The effective mobility is determined as a function of the electric field and charge carrier density $\mu(E, n)$. This is achieved by a potential mapping approach, analyzing a series of current-voltage characteristics of single carrier devices with varying intrinsic layer thicknesses. The evaluation is validated with simulation data, demonstrating that field dependence and charge density dependence can be resolved separately.

The technique is applied to well-established and state-of-the-art material systems. For example, in a blend of zinc phthalocyanine (ZnPc) and Fullerene C60, a field activated hole mobility of $7.9 \cdot 10^{-9} \text{ cm}^2/\text{Vs} \cdot \exp\left(0.01\sqrt{E \cdot \text{cm}/\text{V}}\right)$ is measured.

With this method, the charge carrier mobility can be studied systematically, and the field and charge density dependence upon variations of the chemical composition or the processing conditions can be quantified.

HL 50.8 Wed 11:30 H13

Spectroscopic investigation of air induced charge trapping in n-type polymer semiconductors — ●RICCARDO DI PIETRO¹, TOM B. KEHÖE², and HENNING SIRRINGHAUS² — ¹Institut für Physik und Astronomie, Universität Potsdam, Germany — ²Cavendish Laboratory, University of Cambridge, United Kingdom

We have performed an optical spectroscopy study of how the presence of oxygen and water affects the radical anion charge states in one of the most widely studied electron transporting conjugated polymers, poly{[N,N9-bis(2-octyldodecyl)-naphthalene-1,4,5,8-bis(dicarboximide)-2,6-diyl]-alt-5,59-(2,29-bisthiophene)} (P(NDI2OD-T2)). By combining the results obtained from Charge Accumulation Spectroscopy (CAS)[1], a technique which allows optical quantification of the concentration of charged species in the polymer film, with electrical characterization of P(NDI2OD-T2) organic field-effect transistors (OFETs) we have been able to study the mechanism for bias-stress degradation upon exposure to ambient atmosphere. Here we show that the stability of the polymer anion against water is limited by two competing reactions, one involving the well-known electrochemical oxidation of the polymer anion by water and the other involving a radical anion-catalyzed chemical reaction of the polymer with water leading to degradation of the polymer film.

[1] Di Pietro, R. and Sirringhaus, H. High Resolution Optical Spectroscopy of Air-Induced Electrical Instabilities in n-type Polymer Semiconductors. Adv. Mater. 24 (2012).

HL 50.9 Wed 11:45 H13

Comparing the transition dipole orientation of different phosphorescent emitters in organic light-emitting diodes under electrical excitation — ●PHILIPP LIEHM, CAROLINE MURAWSKI, MAURO FURNO, BJÖRN LÜSSEM, KARL LEO, and MALTE C. GATHER — Institut für Angewandte Photophysik, Technische Universität Dresden, George-Bähr-Str. 1, 01062 Dresden, Deutschland

We investigate the average transition dipole orientation of different phosphorescent matrix/emitter systems that are used in state-of-the-art highly efficient organic light-emitting diodes (OLED). The orientation is determined using two different methods: in-situ angle resolved electroluminescence spectroscopy and analysis of the exciton decay time under electrical excitation. Both methods are supported by optical simulations. We find that the dipoles of the green emitter Ir(ppy)₃ align nearly isotropically in the matrices of TCTA/TPBi and

CBP. By contrast, we show evidence that the Ir(MDQ)₂(acac) and the Ir(ppy)₂(acac) dipoles are preferentially horizontal when embedded in a NPB and a CBP matrix, respectively. Within the range of experimental error, we obtain similar results for both investigated methods. Using optical simulations, we provide a quantitative estimate of how the difference in average orientation influences the external quantum efficiency of OLEDs based on Ir(ppy)₃ and Ir(ppy)₂(acac) embedded in a CBP matrix and compare against experimental results.

HL 50.10 Wed 12:00 H13

Self-passivation of molecular n-type doping during air-exposure using a highly efficient air-instable dopant — ●MAX TIETZE, FLORIAN WÖLZEL, TORBEN MENKE, AXEL FISCHER, BJÖRN LÜSSEM, and KARL LEO — Institut für Angewandte Photophysik, TU Dresden

Since several process steps of organic field effect transistors like photo-lithography cannot be performed in vacuum or inert atmosphere, an application of n-doping with the most efficient molecular n-type dopants is hampered because they are prone to be air-instable due to their low ionization potentials. We study systematically the degradation of films of the n-dopant tetrakis(1,3,4,6,7,8-hexahydro-2H-pyrimido[1,2-a]pyrimidinato)ditungsten(II) (W₂(hpp)₄) on different substrates and doped into C₆₀ films by conductivity measurements, photoelectron spectroscopy, and laser desorption/ionization time of flight mass spectrometry. We find that the conductivity of n-doped C₆₀ layers is restored after air-exposure, if annealed in vacuum. Hereby, the majority of the dopant molecules decompose immediately after air-exposure, whereas the remaining W₂(hpp)₄ molecules stay intact and slowly degrade with an exponential decay time of ≈ 11 min. These findings are explained by passivation of W₂(hpp)₄ molecules, which are in a charge-transfer state and thus protected from further oxidation. Hence, the conservation of the conductivity can be understood in terms of a self-passivation of molecular n-doping and an application of highly efficient n-doped thin films in functional organic devices processed even under ambient conditions is feasible.

HL 50.11 Wed 12:15 H13

using STM/nc-AFM to discriminate adsorbed molecules and attachment geometries on Si(111)-7x7 — ●ZSOLT MAJZIK¹, BENEDICT DREVNIOK², WOJCIECH KAMINSKI³, MARTIN ONDRÁČEK¹, ALASTAIR B. MCLEAN², and PAVEL JELÍNEK¹ — ¹Institute of Physics, Academy of Science of the Czech Republic, Cukrovarnická 10, 162 53, Prague, Czech Republic — ²Queen's University, Kingston, Ontario, Canada, K7L 3N6. — ³University of Wrocław, plac Maksa Borna 9, 50-204 Wrocław, Poland

Scanning tunneling microscopy (STM) has been used to study surface reactions leading to an improved understanding of surface chemistry at the atomic length scale. However, by using a qPlus sensor, non-contact atomic force microscopy (nc-AFM) can be performed at the same time, allowing simultaneous measurement of the tip-surface conductance and tip-surface interaction. Here we present a joined experimental and theoretical study of the adsorption of hydrogen, ethylene and benzene on the Si(111)-7x7. Based on force site spectroscopy combined with density functional theory (DFT) simulations we found that over the molecules and hydrogen only a very weak attractive force appear and mainly the repulsive interaction acts along tip approach. The position of the attractive force maxima on the Z scale and the magnitude of the attractive force can be well used as a fingerprint to discriminate between common defects, such as vacancies, and adsorbates. Moreover, using benzene and ethylene as model systems, we demonstrate that combined STM/AFM provides more information about attachment geometries than STM alone.