

DS 55: Organic Thin Films III

Time: Friday 9:30–12:15

Location: H8

DS 55.1 Fri 9:30 H8

Donor-acceptor molecular interfaces in binary mixtures of organic semiconductors: Diindenoperylene(DIP):[hexafluoro]tetracyanonaphthoquinodimethane([F6]-TCNNQ) vs Sexithiophene(6T):F6TCNNQ — ●GIULIANO DUVA¹, PAUL BEYER², ALEXANDER HINDERHOFER¹, ANDREAS OPITZ², ALEXANDER GERLACH¹, and FRANK SCHREIBER¹ — ¹Universität Tübingen, Institut für Angewandte Physik, Auf der Morgenstelle 10, 72076 Tübingen (Germany) — ²Humboldt-Universität zu Berlin, Department of Physics, Brook-Taylor-Str. 6, 12489 Berlin (Germany)

Binary mixtures of organic semiconductors[1] involve formation of heterointerfaces between materials with different HOMO-LUMO energies. This may lead to partial or integer charge-transfer (CT) between the compounds in the form of either full ionization or frontier orbital hybridization[2]. The different size and shape of the molecular components has a great impact on the structure, leading to complex mixing scenarios from complete phase separation to mixed-crystal formation[1]. Overall, the mixing free energy can be expressed as a function of several parameters involving anisotropic interactions, implicitly taking into account the overlap between frontier orbitals. In this study we combine mixtures of DIP and [F6]TCNNQ with mixtures of 6T and F6TCNNQ in order to vary these parameters and study their impact on the CT. We demonstrate the formation of mixed co-crystal by X-ray scattering, whereas the corresponding CT states are probed by several spectroscopy methods (UV-Vis, IR, Raman).[1]A. Hinderhofer et al. Chem.Phys.Chem.13(2012);[2]H. Méndez et al. Nat.Comm.6(2015)

DS 55.2 Fri 9:45 H8

Correlating the donor/acceptor interface energetics with electronic dynamics in organic bilayer solar cells — ●MICHAEL BRENDEL¹, ESSRAA AHMED², IULIA MINDA², HEINRICH SCHWOERER², and JENS PFLAUM^{1,3} — ¹Exp. Physics VI, Julius-Maximilians-University Würzburg, D-97074 Würzburg — ²Laser Research Institute, Stellenbosch University, ZA-7602 Matieland — ³Bavarian Center for Applied Energy Research (ZAE Bayern), D-97074 Würzburg

The crucial functional building block of any state of the art organic solar cell is the donor/acceptor (D/A) heterojunction. At this interface, the energetic offset of the frontier orbitals between donor and acceptor drives the dissociation of excitons into free charge carriers.

In this contribution we systematically tune the D/A interface energetics of bilayer cells by successive fluorination of the donor material zinc phthalocyanine, $F_n\text{ZnPc}$ ($n = 0, 4, 8, 16$). As evinced by ultraviolet photoelectron spectroscopy, upon fluorination energy levels of the donor are shifted towards lower energies with respect to the acceptor C_{60} . [1] The static picture of interface energetics is complemented by correlation with the excitonic and electronic dynamics accessed via ultrafast transient absorption spectroscopy. Exciton separation at the respective $F_n\text{ZnPc}/\text{C}_{60}$ interface takes place on fs-time scale, increasing in speed with increasing energetic offset at the D/A interface. After initial exciton dissociation, recombination dynamics of electrons in C_{60} remain almost unaffected by the D/A interface energetics on a ps-time scale. Financial support from SOLTECH and the DAAD.

[1] M. Brendel et al., Adv. Funct. Mater., 2015, 25, 1565.

DS 55.3 Fri 10:00 H8

Effects of Molecular Orientation in Acceptor-Donor Interfaces between Pentacene and C_{60} and Diels-Alder Adduct Formation at the Molecular Interface — ●TOBIAS BREUER, ANDREA KARTHÄUSER, and GREGOR WITTE — AG Molekulare Festkörperphysik, Philipps-Universität Marburg

Interfaces between pentacene and Buckminster-Fullerene (C_{60}) have attracted interest due to their application as oligomeric model system for organic solar cells. As the actual device characteristics in such implementations are crucially controlled by the interface structure, detailed investigations of this interface on a molecular level are mandatory. Therefore, we have analyzed the influence of the orientation of the pentacene molecules in highly-ordered crystalline bottom layers on the characteristics of such interfaces. We show that the interface structure is driven by temperature-controlled diffusion of C_{60} molecules to the pentacene step-edges in the case of uprightly-oriented pentacene. For lying pentacene in the bottom layer, no step-edge decoration is observed and the wetting of the pentacene layer is enhanced.

Furthermore, the stability of the interface against intercalation and re-orientation has been analyzed by means of NEXAFS spectroscopy, showing that the orientation of the pentacene molecules at the interface remains unchanged. Instead, we observe strong indication for a chemical modification of the molecular entities by the formation of Diels-Alder adducts between C_{60} and pentacene, which challenges the interpretation of this model system as chemically inert.

DS 55.4 Fri 10:15 H8

The energy level alignment at the interfaces of CoPc with ferromagnetic substrates studied by ultraviolet and inverse photoemission spectroscopies — ●JING GUO, VOLODYMYR DZHAGAN, GEORGETA SALVAN, and DIETRICH R.T. ZAHN — Semiconductor Physics, Technische Universität Chemnitz, 09107 Chemnitz Germany

Metal-organic interfaces play a crucial role for the ever growing field of organic spintronics. Here the electronic structure of the interface between a CoPc thin film and Co or Ni foils as substrates is investigated by ultraviolet photoemission spectroscopy (UPS) and inverse photoemission spectroscopy (IPES). Both HOMO and LUMO positions of CoPc are noticeably dependent on the CoPc film thickness. Due to the image charge screening effect induced by the metallic substrate, the positions of LUMO and HOMO both shift towards lower binding energy at the interface. In addition, an interfacial state is supposed to form at the CoPc/Co interface, but not in the case of the CoPc/Ni interface. As a result, the transport band gap of CoPc on Co foil "opens" from (1.3 ± 0.3) eV at 1 nm film thickness up to (2.2 ± 0.3) eV above 6 nm film thickness. But for CoPc on Ni foil, its "opening" is much less pronounced from (1.9 ± 0.3) eV to (2.2 ± 0.3) eV. This different energetic behaviour at these interfaces is important for designing the electronic and spintronic devices.

DS 55.5 Fri 10:30 H8

The role of Induced Density of Interface States in the Interfacial Energy Level Alignment of PTCDA — ●MAHDI SAMADI KHOSHKKHO¹, HEIKO PEISERT¹, THOMAS CHASSÉ^{1,2}, and MARCUS SCHEELE^{1,2} — ¹Institute of Physical and Theoretical Chemistry, University of Tübingen, Auf der Morgenstelle 18, 72076 Tübingen, Germany — ²Center for Light-Matter Interaction, Sensors & Analytics LISA+, University of Tübingen, Auf der Morgenstelle 15, 72076 Tübingen, Germany

We use various type of diverse substrates with different work functions and different coupling interactions to investigate the electronic structure of PTCDA using ultraviolet and X-ray photoelectron spectroscopy (UPS and XPS) as well as complementary electrostatic potential calculations. For thick enough layers of PTCDA, nearly unchanged injection barriers on all substrates are observed without any dependence on the type of substrate (unreactive, reactive or passivated metals and polymers). The Fermi level is observed to be strongly pinned at the charge neutrality level (CNL) of the organic semiconductor. For lower thicknesses of PTCDA, this universal Fermi level pinning is perturbed and differences in the work function of up to 0.8 eV are detected, depending on the nature of the substrate and the thickness. We find near-quantitative agreement between our experimental data and electrostatic potential calculations in the framework of an expanded model of induced density of interface states (IDIS). These results provide valuable information for the design and fabrication of PTCDA-based heterostructures.

15 min. break.

DS 55.6 Fri 11:00 H8

The energy levels in hole-doped molecular semiconductors — ●PATRICK AMSALEM¹, STEFANIE WINKLER^{1,2}, JOHANNES FRISCH¹, MARTIN OEHZELT^{1,2}, GEORG HEIMEL¹, and NORBERT KOCH^{1,2} — ¹Institut für Physik & IRIS Adlershof, Humboldt-Universität zu Berlin — ²Helmholtz-Zentrum Berlin für Materialien und Energie GmbH

Understanding the energy level alignment in doped organic thin films is crucial in order to achieve rational design in opto-electronic organic devices. Here, we rely on interface doping phenomena as occurring at electrode / buffer layer / organic semiconductor to hole-dope a ultra-thin film C_{60} [1]. The present system is investigated by direct and inverse photoemission measurements and theoretical calculations

based on density functional theory. The obtained results reveal a picture which differs strongly from the traditionally conceived one, i.e. where the energy levels consist of singly occupied molecular states lying within the energy gap of the semiconductor [2]. Instead, here we demonstrate that the on-site Coulomb repulsion splits the partially unoccupied frontier molecular level in the p-doped systems into two sub-levels [1]. The role of inter-site Coulomb interaction between molecular ions and neighbor molecules is further addressed and helps providing a complete picture of the electronic structure of molecular semiconductors in the presence of excess charges [1]. [1] S. Winkler, P. Amsalem, J. Frisch, M. Oehzelt, G. Heimel, N. Koch, *Materials Horizons* 2 (2015) 427. [2] J. L. Bredas and G. B. Street, *Acc. Chem. Res.* 18 (1985) 309.

DS 55.7 Fri 11:15 H8

Characterization of charge transfer in weakly interacting organic mixtures — ●VALENTINA BELOVA¹, ALEXANDER HINDERHOFER¹, ALEXANDER GERLACH¹, FRANK SCHREIBER¹, EDUARD MEISTER², WOLFGANG BRÜTTING², PAUL BEYER³, and ANDREAS OPITZ³ — ¹Institut für Angewandte Physik, Universität Tübingen, Germany — ²Institut für Physik, Universität Augsburg, Germany — ³Institut für Physik, Humboldt-Universität zu Berlin, Germany

To obtain a detailed understanding of the structural and energetic aspects of intermolecular interaction upon mixing we study the CT in thin films of DIP and PEN as donors and PDIR-CN2 and PDIF-CN2 as acceptors, which are relevant for organic electronic devices[1]. Mixing rigid rod-like materials (DIP, PEN) with a compound with flexible alkyl-chains (PDIR-CN2, PDIF-CN2) give rise to many different structural configurations between both species. Choosing the components in binary molecular mixtures[2] we adjust the energy gap between the donor HOMO level and the acceptor LUMO level. We characterize the CT of these mixtures upon electronic excitation (via PL and optical absorption) as well as at the ground-state (via FTIR) in combination with X-ray scattering to define the correlation with structural properties and anisotropic character of the CT.

[1] P.J. Jadhav et.al. *Adv. Mater.*, 24, 6169 (2012); [2] A. Hinderhofer/F. Schreiber, *ChemPhysChem*, 13, 628 (2012)

DS 55.8 Fri 11:30 H8

Controlled UHV growth of organic-inorganic hybrid structures: Conjugated molecules on ZnO — ●MINO SPARENBERG¹, ANTON ZYKOV¹, JÖRG MEGOW¹, VIOLA SCHMIDT¹, YVES GARMSHAUSEN², STEFAN HECHT², STEFAN KOWARIK¹, and SYLKE BLUMSTENGEL¹ — ¹Humboldt Universität zu Berlin, Institut für Physik — ²Humboldt Universität zu Berlin, Institut für Chemie

For the fabrication of inorganic-organic hybrid structures an understanding of the interaction at the interface is crucial. Therefore the growth of thin organic films is conducted in an all-UHV MBE system and analysed *in situ* via AFM and differential reflectance spectroscopy (DRS). The inorganic semiconductor examined here is epitaxially grown ZnO. Studied is the influence of chemical tuning on the growth process using the organic molecule *para*-sexiphenyl (6P). As promising candidate for usage in opto-electronic devices controlling the growth properties is critical [*Phys. Rev. B*, 2008, 77, 085323]. For this chemical tuning is used, as done for 6P by partial fluorination. We show that due to different terminal fluorination of 6P the growth mode could be drastically changed. Whereas symmetric fluorinated 6P-F₄

shows a smooth layer-by-layer growth [PCCP, 2014, 16, 26084], asymmetric 6P-F₂ possesses a static dipolar moment making it sensitive to the surface of ZnO. Furthermore the growth of PTCDI and NTCDA were investigated via DRS where the evolution of thin PTCDA films from monomer to aggregate was observed and successfully theoretically described [*J. Phys. Chem. C* 2015, 119, 5747] whereby for NTCDA the resonant overlap at the edge of ZnO is observed.

DS 55.9 Fri 11:45 H8

Organic-inorganic nanocomposites: nano-crystals of Au, Al and Ag in CuPcF4 organic molecular film — ●SERGEY BABENKOV¹, OLGA MOLODTSOVA^{1,2}, ANDREI HLOSKOVSKY¹, IRINA ARISTOVA³, MAXIM TCHAPLYGUINE⁴, RALF NYHOLM⁴, KARINA SCHULTE⁴, DENIS VYALIKH⁵, OLEG VILKOV⁵, and VICTOR ARISTOV^{1,3,6} — ¹DESY, Hamburg, Germany — ²ITMO, Saint Petersburg, Russia — ³ISSP RAS, Chernogolovka, Russia — ⁴Max-lab, Lund, Sweden — ⁵BESSY, Berlin, Germany — ⁶TU Bergakademie, Freiberg, Germany

The morphology and electronic properties of nano-composite films based on blended aluminum, gold and silver nanoparticles into organic semiconductor of fluorinated copper phthalocyanine (CuPcF₄) have been investigated by means of TEM and SR-PES measurements as function of nominal amount of metal deposition. TEM measurements reveal organic film with self-assembled nanoparticles, whose size and distribution are strongly correlated with nominal amount of deposited metal. Moreover, comparative study of electronic properties self-assembled nanoparticles detects strong interaction of metal atoms with organic substrate. This work was supported by the RFBR Grant No. 13-02-00818 and the BMBF-Project No. 05K12GU2, PSP-Element No. U4606BMB1211.

DS 55.10 Fri 12:00 H8

μ -Photoluminescence studies on the interaction between charge carriers and excitonic states in organic semiconductors — ●T. FERSCHKE¹, N.H. HANSEN¹, T. SCHMEILER¹, and J. PFLAUM^{1,2} — ¹Experimental Physics VI, Julius Maximilian University, 97074 Würzburg — ²ZAE Bayern, 97074 Würzburg

Charge carrier – exciton interactions are of significant importance for the performance of organic opto-electronic devices.[1] Recently, it has been shown that the current density in an organic semiconducting matrix can be analyzed on nanometer length scales by means of the photoluminescence (PL) of single guest dye molecules.[2] Here, we transfer the aforementioned concept from single molecules to, technologically more relevant, molecular ensembles by utilizing μ -PL studies to characterize intentionally doped Tris(8-hydroxyquinolinato)aluminium (Alq₃) organic light emitting diodes (OLEDs). For this purpose, Tetraphenylidibenzoperiflanthene (DBP) was embedded as dopant (0.1 wt%) via vacuum deposition at vertically defined positions within the Alq₃ emitting layer. Upon applying a negative bias to the Ca/Al cathode, we observe an effective reduction in the PL of DBP by up to 14%. Varying the vertical position of the dopant and performing a 2D μ -PL-mapping we gain comprehensive information on the static and dynamic charge carrier characteristics within the recombination zone. These data provide insights in the microscopic mechanisms governing the two competing processes of PL quenching and electroluminescence.

[1] N.H. Hansen, *et al.*, *Phys. Rev. B*, **2013**, 87, 241202(R)

[2] M. Nothaft, *et al.*, *ChemPhysChem*, **2011**, 12, 2590–2595