

HL 63: Organic electronics and photovoltaics III (O, jointly with CPP, DS, HL)

Time: Wednesday 16:00–19:00

Location: H33

HL 63.1 Wed 16:00 H33

Effects of nuclear dynamics on light absorption, charge injection, recombination, and dye regeneration conditions in dye-sensitized solar cells — ●SERGEI MANZHOS¹, HIROSHI SEGAWA², and KOICHI YAMASHITA³ — ¹Department of Mechanical Engineering, National University of Singapore, Blk EA #07-08, Singapore 117576 — ²RCAST, University of Tokyo, 4-6-1, Komaba, Meguro-ku, Tokyo 153-8904, Japan — ³Department of Chemical System Engineering, University of Tokyo, 7-3-1, Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

We present molecular dynamics studies of effects of nuclear motions on light absorption and charge injection, recombination, and dye regeneration conditions for two organic dyes adsorbed on anatase (101) surface of TiO₂ in mono- and bi-dentate configurations. We studied the effects of temperature, deuteration, and co-adsorbed water. Averaged over nuclear motions driving forces for injection and regeneration can differ significantly from their static estimates computed in most works. As a result, injection rate could be different by orders of magnitude. As the expectation value of the ground state energy is higher than its optimum geometry value (by up to 0.1 eV), nuclear motions will affect dye regeneration by recently proposed redox shuttle-dye combinations operating at low driving forces. Dye orientation motions are predicted to increase back-donation rate by orders of magnitude. Dye structure, adsorption mode, and the presence of water affect strongly the dynamics of energy level matching. Temperature in the range of 300-350K and deuteration have little effect on driving forces but red-shift of the absorption spectrum by a few %.

HL 63.2 Wed 16:15 H33

Photoemission Studies of Highly Reactive Organic Photosensitizers — ●MATHIAS FINGERLE¹, MAXIMILIAN HEMGESBERG², YVONNE SCHMITT², SEBASTIAN SCHMITT², DIMITRI IMANBAEW², HARALD KELM², EUGEN RISTO², STEFAN LACH¹, MARKUS GERHARDS², CHRISTOPH VAN WÜLLEN², WERNER THIEL², and CHRISTIANE ZIEGLER¹ — ¹Fachbereich Physik, Erwin-Schrödinger-Str. 56, D-67663 Kaiserslautern, Germany — ²Fachbereich Chemie, Erwin-Schrödinger-Str. 52, D-67663 Kaiserslautern, Germany

Substituted phenothiazines (PTs) are promising candidates for applications in the field of organic electronics. Due to the fact, that the electronic, magnetic and geometrical properties of the phenothiazine compared to its radical cation differ substantially, PT redox couples are of great interest for organic devices like dye sensitized solar cells (DSSCs). Here, the electronic properties of N-substituted phenothiazine dyes derived from 3,8-dithien-2-ylphenothiazine (DTPT), among them the first PT containing an olefinic moiety with an electron withdrawing group close to the nitrogen atom, were probed via photoemission spectroscopy. The thin film growth of the dyes and their oxidized species after spin coating was analyzed by X-ray photoelectron spectroscopy (XPS) and qualitatively visualized by scanning force microscopy (SFM). Through UV-photoelectron spectroscopy (UPS) and inverse photoelectron spectroscopy (IPES), the occupied and unoccupied energy levels could be attained and compared to data acquired by UV/Vis spectroscopy and DFT calculations. It is shown, that chemical oxidation by NOBF₄ leads to a dramatic decrease of the band gap.

HL 63.3 Wed 16:30 H33

Investigation of the electronic structure of phosphorescent Platinum(II) complexes on Au(111) by STM and STS — ●PASCAL RAPHAEL EWEN, HASMIK HARUTYUNYAN, JAN SANNING, MATTEO MAURO, CRISTIAN ALEJANDRO STRASSERT, and DANIEL WEGNER — Physikalisches Institut - Westfälische Wilhelms Universität Münster

Quenching effects still limit the efficiency of state-of-the-art organic light emitting diodes (OLEDs) at higher doping concentrations of the triplet emitter molecules within the emission layer. A possible candidate for avoiding of the loss of luminescence are recently synthesized Pt(II) complexes that do not show quenching even when aggregated into fibers or gels. The efficient implementation of such complexes in electronic devices requires a fundamental understanding of the interaction of the molecules with the local environment. A systematic investigation of the adsorption and the electronic structure of slightly different phosphorescent Pt(II) complexes offers information about the influence of ligands and substituents on the complexes as well as their interac-

tions with neighbours and the substrate. We have studied the impact of molecule-surface and intermolecular interactions on the self-assembly and electronic structure of Pt-complex monolayers on Au(111) using scanning tunneling microscopy (STM) and spectroscopy (STS) at low temperature. By determining energies and spatial distributions of several frontier orbitals, we are able to evaluate the impact of hybridization on the molecular electronic structure with important consequences for the optical properties.

HL 63.4 Wed 16:45 H33

Overcoming the limitations of work-function modifications induced by adsorption of self-assembled monolayers — ●OLIVER T. HOFMANN, YONG XU, PATRICK RINKE, and MATTHIAS SCHEFFLER — Fritz-Haber Institut der MPG, Berlin, Germany

Controlling the work function of electrodes critically determines charge-injection barriers and is of high importance for organic electronic devices. Such control can be easily achieved by adsorbing dipolar self-assembled monolayers. Despite the common application of this method, its limitations remain largely unexplored. It has, however, been demonstrated that charge-transfer occurs as soon as the molecular LUMO comes into resonance with the Fermi-energy when the molecular dipole moment is systematically increased by adding multiple repeat units. This Fermi-level pinning limits the achievable work-function modification. In turn, we argue that molecules with negative electron affinities never reach this limit and can reduce the work-function in principle all the way down to zero. As a proof of concept, we study the interaction between the ZnO(10 $\bar{1}$ 0) surface and pyridine using hybrid density functional theory with a variable fraction of exact exchange and a correction scheme for screened van-der-Waals forces. In agreement with experimental observations, we find an adsorption-induced work-function reduction of up to -2.9 eV. For a hypothetical ultra-dense pyridine monolayer the work-function reduction could even reach -4.3 eV for this surface.

HL 63.5 Wed 17:00 H33

Surface electronic structure and electron dynamics for pristine and adsorbate-covered ZnO(10 $\bar{1}$ 0) — ●JAN-CHRISTOPH DEINERT, DANIEL WEGKAMP, MICHAEL MEYER, JULIA STÄHLER, and MARTIN WOLF — Fritz-Haber-Institut der MPG, Abt. Physikalisches Chemie, Faradayweg 4-6, 14195 Berlin

Zinc oxide is a promising electrode material for organic optoelectronics, because of its large optical band gap, possible n-type conductivity and its abundance. Despite many years of research, the electronic structure of interfaces between ZnO and - possibly functional - molecules or even its vacuum interface are not well understood. We use femtosecond time- and angle-resolved two-photon photoemission spectroscopy (2PPE) to analyze both the occupied and unoccupied electronic states and dynamics at such interfaces. We show that hydrogen adsorption, even for very low coverage, leads to the formation of a surface electron accumulation layer and thus surface metallicity. Above band gap excitation with 3.8 eV fs laser pulses leads to ultrafast relaxation of hot electrons in the ZnO(10 $\bar{1}$ 0) conduction band and the alleged formation of an excitonic state with a lifetime in the 100 ps range. Furthermore, we demonstrate that molecules with negative electron affinity allow for massive work function reduction of ZnO(10 $\bar{1}$ 0), e.g. by $\Delta\Phi = -2.9$ eV in the case of a monolayer of pyridine. This opens a pathway to the design of cathodes with optimal electron injection barriers. We furthermore examine the changes in interfacial electronic structure upon biphenyl adsorption, which serves as a model system for optoelectronically functional poly(*p*-phenylene)-type molecules.

HL 63.6 Wed 17:15 H33

Defect-Driven Interfacial Electronic Structure at a Hybrid Organic / Inorganic Heterojunction — ●OLIVER MONTI¹, LEAH KELLY¹, LAURA SCHIRRA¹, PAUL WINGET², HONG LI², and JEAN-LUC BREDAS² — ¹The University of Arizona, Tucson, AZ, USA — ²Georgia Institute of Technology, Atlanta, GA, USA

We present a combined experimental and theoretical study of the interfacial electronic structure of highly defined thin films of organic semiconductors on ZnO. We discuss the importance of shallow donor states in the near-surface region of ZnO in determining energy-level alignment and electronic structure at such interfaces. Using ultravi-

olet and x-ray photoelectron spectroscopy together with two-photon photoemission and first-principles calculations we investigate the nature of hybrid interface states inside the bandgap of ZnO. These states display strong charge-transfer character and may play an important role in charge-harvesting events in organic photovoltaic cells.

HL 63.7 Wed 17:30 H33

Electronic structure and excited states dynamics in polythiophene — ●LEA BOGNER¹, GAURAV GUPTA², MICHAEL SOMMER³, MUKUNDAN THELAKKAT⁴, THOMAS THURN-ALBRECHT², and PETRA TEGEDER^{1,5} — ¹Freie Universität Berlin, Fachbereich Physik — ²Martin-Luther-Universität Halle-Wittenberg, Institut für Physik — ³Albert-Ludwigs-Universität Freiburg, Institut für Makromolekulare Chemie — ⁴Universität Bayreuth, Makromolekulare Chemie I — ⁵Rubrecht-Karls-Universität Heidelberg, Physikalisch-Chemisches Institut

Semiconducting conjugated polymers exhibit promising properties for applications in optoelectronic devices such as organic photovoltaic cells. Poly(3-hexylthiophene) (P3HT) and other poly- and oligothiophenes are auspicious electron donor materials due to their high charge carrier mobility. In this study thin films of semi crystalline P3HT with different degree of crystallinity [1] have been investigated by means of time- and angle-resolved two-photon photoemission (2PPE). We observed several unoccupied and occupied electronic states (bands) including the valence and conduction band. In addition two excited states are found which possess lifetimes in the order of hundred picoseconds.

Ref.: [1] Z. Wu, A. Petzold, T. Henze, T. Thurn-Albrecht, R. H. Lohwasser, M. Sommer, M. Thelakkat, *Macromolecules*, 2010, 43, 4646-4653.

HL 63.8 Wed 17:45 H33

Charge transfer at the interface between substituted pentacene nanorods and gold single crystals — ●SABINE-ANTONIA SAVU, MARIA BENEDETTA CASU, and THOMAS CHASSÉ — Institute of Physical and Theoretical Chemistry, University of Tübingen, Tübingen, Germany

Pentacene is one of the most investigated organic molecules due to its successful application in organic electronics. Substitution in pentacene gives the opportunity to tailor the properties which are needed for applications; therefore it is necessary to investigate its influence on molecular aggregation and thin film formation. In particular, here we report our investigations on nanorods of three newly synthesized substituted pentacenes with different degrees of fluorination. We performed X-ray photoemission spectroscopy (XPS), near edge X-ray absorption fine structure (NEXAFS) spectroscopy, and atomic force microscopy (AFM) on nanorods deposited on Au(111) and Au(110) single crystals. XPS thickness dependent spectra in combination with NEXAFS investigations show that the screening of the core hole occurs via charge transfer from the metal to the molecule. In addition, the morphology of the nanorods has been investigated by using AFM, evaluating the nanorod characteristics also from a statistical point of view and taking the different degree of fluorination into account.

HL 63.9 Wed 18:00 H33

Photoemission Investigation of the Electronic Structure of P3HT:PCBM Bulk-Heterojunctions using a lift-off technique — ●ANGELA ECKSTEIN^{1,2}, DIRK HAUSCHILD^{1,2}, JULIA KERN³, MARKUS MINGEBACH³, CARSTEN DEIBEL³, VLADIMIR DYAKONOV³, ACHIM SCHÖLL^{1,2}, and FRIEDRICH REINERT^{1,2} — ¹Experimentelle Physik VII, Universität Würzburg, 97074 Würzburg — ²Gemeinschaftslabor für Nanoanalytik, Karlsruher Institut für Technologie KIT, 76021 Karlsruhe — ³Experimentelle Physik VI, Universität Würzburg, 97074 Würzburg

Poly(3-hexylthiophene): phenyl-[6,6]-C61 butyric acid methyl ester (P3HT:PCBM) bulk heterojunctions (BHJ) are prototype active layers for organic solar cells. The electronic structure at the internal interface can be accessed by photoelectron spectroscopy (PES), thus providing insight into the alignment of the electronic levels and the occurrence of possible interface dipoles. However, the very surface sensitive PES investigation is complicated in case of P3HT:PCBM bulk heterojunctions since the film preparation by spin-coating creates a P3HT wetting layer on the film surface. In order to avoid this problem we used a lift-off technique to access the interface to the spin coating substrate (SiO₂), which has shown to resemble the bulk situation [1]. P3HT:PCBM samples with different mixing ratio, which can be lift-off-prepared under UHV-condition thus avoiding contamination by ambient conditions, have been investigated by x-ray- and UV-PES

as well as by inverse PES with particular respect to the influence of degradation and radiation damage. [1] Kahn et al. (*Org. El.* 11 (2010) 1779-1785)

HL 63.10 Wed 18:15 H33

Bottom-up synthesis of self-aligned conjugated polymers — SÖREN KROTZKY¹, ●RICO GUTZLER¹, VIJAY VYAS^{1,2}, BETTINA LOTSCH^{1,2}, and KLAUS KERN^{1,3} — ¹Max Planck Institute for Solid State Research, Stuttgart, Germany — ²Department of Chemistry, University of Munich (LMU), Munich, Germany — ³Institut de Physique de la Matière Condensée, Ecole Polytechnique Fédérale de Lausanne, Switzerland

We investigate the synthesis of self-assembled organometallic structures and well-defined long 1D polymers by the surface-supported Ullmann reaction on an Ag(111) surface. The brominated semiconducting precursor molecule (2,7-dibromobenzothieno[3,2-b]benzothiophene) is sublimed under UHV conditions on the crystalline surface where a dehalogenation step is induced at room temperature. STM reveals self-assembly of the dehalogenated ditopic molecule into short organometallic coordination polymers that arrange in a ladder-like monolayer. Annealing to 420 K leads to C-C coupling of the molecules via ejection of the coordinated metal atom. At this temperature the newly formed 1D polymer strands align in a side-by-side manner with three preferred directions with respect to the high-symmetry directions of the surface. DFT calculations show that the length of the synthesized polymers is sufficient to reduce the HOMO-LUMO gap to its value at infinite length of the polymer. Together with the calculated band-structure this suggests possible unidirectional charge mobility within the well-ordered semiconducting polymeric monolayer.

HL 63.11 Wed 18:30 H33

How contact groups influence metal molecule hybrid structures under voltage — ●SIMON LIEBING, TORSTEN HAHN, and JENS KORTUS — TU Bergakademie Freiberg, Freiberg, Germany

In order to use molecules in electronics it is not only important to understand the properties of molecules themselves but also properties of metal-molecule interfaces. Recent contributions discussed the behavior of thiols [1] and amino linker groups [2]. To get a more systematic understanding the authors have chosen a model system of benzene with variable linker groups between gold electrodes. Such groups can be thiole, amino, thiophen, nitrile, pyrrol and cyanide. This allows for example to study the differences between σ - and π - like symmetry with respect to the individual interface geometry. The theoretical study combines the calculation of single molecule properties by density functional theory [3] with the nonequilibrium Greens functions technique [4] to calculate the transport properties [5] of the device. [1] Markussen, T. et al. *JCP* **132**, 224104 (2010)

[2] Angela, D. et. al. *Nano Letters* **10**, no. 7 (2010)

[3] Pederson, M. et. al. *Phys. Status Solidi b* **217**, 197. (2000)

[4] Datta, S. *Nanotechnology* **15**, 433. (2004)

[5] Brandbyge, M. *Phys. Rev. B* **65**, 165401 (2002)

HL 63.12 Wed 18:45 H33

Improving the contact materials of organic electronic devices: Polymeric dipole layers vs. self assembling monolayers — ●JANUSZ SCHINKE^{1,2}, JULIAN HEUSSER^{3,2}, MARC HÄNSEL^{3,2}, JULIA MAIBACH^{4,2}, WOLFGANG KOWALSKY^{1,2}, MICHAEL KRÖGER^{1,2}, ERIC MANKEL^{4,2}, and WOLFRAM JÄGERMANN^{4,2} — ¹TU Braunschweig, Institut für Hochfrequenztechnik — ²Innovation Lab GmbH — ³Universität Heidelberg, Kirchhoff-Institut für Physik — ⁴TU Darmstadt, Materials Science Institute, Surface Science Division

In organic electronic devices, charge injection at the contacts is crucial for high electrical performance. Most of these devices require at least one electrode with a sufficiently low work function (WF). Low-WF electrodes like alkaline earth metals are easily available; however, they are chemically very reactive and oxidize in ambient atmosphere. A smart way to overcome this problem is the use of molecular or polymeric dipole layers (PDLs). The use of PDLs to tune an electrodes work function can be advantageous over self assembled monolayers(SAMs) as the PDL concept can be applied to a wider range of electrode materials like ITO, Ag, Au or Al. We have used two different PDLs: branched polyethylenimine (PEI) and polyethyleneimine ethoxylate (PEIE). We studied the the properties of PDL treated substrates via AFM, ambient Kelvin probe and XPS/UPS. Both interlayers lower the metal substrate work function by approx. 1000meV. On ITO we reach absolute values of about 3.0eV which leads to strongly enhanced electron injection in model devices.