

O 85: Organic-Inorganic Systems IV: Electronic Structure

Time: Thursday 15:00–18:00

Location: S051

Invited Talk

O 85.1 Thu 15:00 S051

Electrostatic Design of Organic Materials and Hybrid Interfaces — ●EGBERT ZOJER — Institute of Solid State Physics, NAWI Graz, Graz University of Technology, Petersgasse 16, 8010-Graz, Austria

In hybrid organic/inorganic interfaces collective electrostatic effects often determine electronic properties like the relative alignment of electronic states, adsorption-induced changes in the work-function, XPS shifts and ballistic transport properties. Here, we suggest ways of intentionally employing these effects for realizing new types of electrostatically designed nanoscopic materials. This includes the development of a modular and versatile toolbox for realizing complex interfacial structures like monolayer quantum-cascades or quantum-well structures. It also comprises the use of polar adsorbates on layered van-der Waals bonded materials like graphene or layered semiconductor structures with the aim of locally concentrating charge carriers for an adsorbate-driven patterning of conductive channels. Finally, I will address possibilities for electrostatically designing the energy landscape of self-assembled three-dimensional organic networks with possible applications in charge carrier separation or carrier injection.

O 85.2 Thu 15:30 S051

Electronic structure of charge transfer salts: application of self-interaction corrected density functional theory — ●TORSTEN HAHN¹, TORSTEN HAHN², and TORSTEN HAHN² — ¹Institute for Theoretical Physics, TU Freiberg, 09599 Freiberg, Germany — ²IFW Dresden, Helmholtzstraße 20, 01069 Dresden, Germany

We present our experimental and theoretical results on novel Picene/F4TCNQ and Manganese-Phthalocyanine/F4TCNQ donor / acceptor systems. We apply the recently developed Fermi-orbital based approach for self-interaction corrected density functional theory (FO-SIC DFT) to these materials and compare the results to standard DFT calculations [1,2,3]. Further we compare the theoretical results with experimental data obtained by photoemission spectroscopy. We focus our analysis on the comparison of orbital eigenvalues, ionization potentials and the magnitude of the ground state charge transfer. We show that for weakly bound donor / acceptor systems the FO-SIC approach delivers results closer to experiment compared to standard DFT calculations.

- [1] T. Hahn et al., J. Chem. Phys. (accepted: AIPID 029546JCP).
- [2] M. R. Pederson, A. Ruzsinszky, and J. P. Perdew, J. Chem. Phys. 140, 121103 (2014).
- [3] M. R. Pederson, J. Chem. Phys. 142, 064112 (2015).

O 85.3 Thu 15:45 S051

Structural and electronic properties of organic charge-transfer complexes on Ag(111) — ●KATHRIN MÜLLER^{1,2}, NICO SCHMIDT¹, MICHAEL GRUNST³, RENE RIEDEL³, MILAN KIVALA³, and MEIKE STÖHR¹ — ¹Zernike Institute for Advanced Materials, University of Groningen, Netherlands — ²Max Planck Institute for Solid State Research, Stuttgart, Germany — ³Department of Chemistry and Pharmacy, University Erlangen-Nürnberg, Germany

The use of organic molecules in electronic devices is gaining increasing interest due to their low cost, flexibility and easy processability. However, organic molecules often show weak intermolecular interactions limiting the electron mobility of organic films. One way to overcome these problems is the use of complementary molecules, which exhibit a strong intermolecular interaction. We employ molecules with complementary functional groups as well as complementary building blocks, e.g. by using electron rich and electron poor building blocks. In this work, we studied the self-assembly and the electronic properties of two molecules containing cyano- and methoxy-groups, respectively, on a Ag(111) surface. The cyano-functionalized molecule exhibits a high electron affinity, while the other one shows a low ionization potential. The investigations of the structural and electronic properties of the individual species as well as the mixed layer were carried out by scanning tunneling microscopy and spectroscopy, X-ray and ultraviolet photoelectron spectroscopy and low-energy electron diffraction. We found that the electronic properties of the mixed layer are changed with respect to the assemblies containing one molecular species.

O 85.4 Thu 16:00 S051

Electronic Structure of TIPS-Pentacene on Au(111) — ●ARNULF STEIN and PETRA TEGEDER — Physikalisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg, Germany

Functionalized Oligoacenes have moved into the field of view for applications in organic electronic devices during the last years. One representative of this group of organic semiconductors is the triisopropylsilylethynyl-pentacene (TIPS-Pc) which stands out because it combines solubility, self-assembly into π -stacked arrays to enhance intermolecular orbital overlap [1] and vacuum processability [2]. Furthermore it can undergo a singlet fission process [3], which is one possibility to overcome the theoretical Shockley Queisser - Limit. We investigated the TIPS-Pc/Au(111) interface by means of two-photon-photoemission (2PPE) which is one of the most powerful tools to elucidate electronic structures and dynamics of optically excited states at interfaces and within thin films.

- [1] J.E. Anthony *et al.*, JACS, 123, 9482 (2001).
- [2] A. Gnoli *et al.* J. Phys. Chem. C, 118, 22522 (2014).
- [3] A. J. Musser *et al.* Nat. Phys. 11, 352 (2015).

O 85.5 Thu 16:15 S051

Charge transport across interfaces between metals and disordered-semiconductors — PHILIPP BREITEGGER¹, MARKUS KRAMMER¹, CHRIS GROVES², and ●KARIN ZOJER¹ — ¹Institute of Solid State Physics and NAWI Graz, Graz University of Technology, Graz, Austria — ²School of Engineering and Computing Sciences, Durham University, United Kingdom

Injection of charges from the metal contacts into organic semiconductors, i.e., de facto insulators, is crucially determining the performance of organic devices. Reaching an in-depth understanding of fundamental processes occurring when a steady-state electric current passes the interface, is an indispensable step towards truly active control of charge transport, e.g., by manipulating both interface and semiconductor via intentional doping. To conceive a model being strictly based on the injection barrier, the shape of the density of states, and the external bias, we utilize Kinetic Monte Carlo simulations to identify conditions leading to ohmic or space charge limited currents, i.e., currents being exclusively determined by the semiconductor. A fraction of charges entering the semiconductor is immobilized at the interface such that the Fermi level becomes aligned with the semiconductors transport energy at the interface. Owing to this alignment, further carriers are injected resonantly and contribute to the current. On the basis of these findings, we formulate a necessary condition to obtain bulk-limited current irrespective of the injection barrier.

O 85.6 Thu 16:30 S051

Characterizing Charge-Transfer Effects at Metal/Organic Interfaces by means of Two-Photon Photoemission — ●DAVID GERBERT and PETRA TEGEDER — Physikalisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg, Deutschland,

Further progress in the field of organic electronic devices requires a fundamental understanding of metal/molecule interactions at the interface between organic semiconducting materials and metal electrodes. These metal/molecule interactions lead to an energetic realignment, including the formation of new states and even bands, which may act as a basis for a improved device performance [1]. Two-photon photoemission (2PPE) is a powerful tool which enables the observation of occupied and unoccupied electronic states directly at the interface. Additionally 2PPE experiments can be performed in a time-resolved or angle-resolved manner to gain insights into dynamics of optically excited electronic states and possible delocalized charge-carriers.

In this talk I will show recent results of different adsorbate/metal interfaces indicating adsorption-induced energetic realignment and band formation.

- [1] M. Wiefner *et al.*, Nat- Commun. 2013, 4, 1514.

O 85.7 Thu 16:45 S051

Excitation dynamics at the PTCDA/TiOPc heterointerface on Ag(111) — ●ALEXANDER LERCH¹, FREDERIK SCHILLER^{1,2}, and ULRICH HÖFER¹ — ¹Fachbereich Physik und Zentrum für Materialwissenschaften, Philipps-Universität, D-35032 Marburg — ²Centro de Física de Materiales, San Sebastian, Spain

The charge carrier transport across metal/organic and organic het-

erointerfaces was investigated by means of time-resolved two-photon photoemission (2PPE). We deposited well defined layers of perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA) on top of titanylphthalocyanine (TiOPc) on an Ag(111) substrate as model system. An optical parametric oscillator (OPO) provided tuneable pump pulses with photon energies ranging from 1.6 to 2.5 eV. Excitons in PTCDA and TiOPc were excited selectively and the subsequent charge transfer to the metal was monitored by photoemission with 4.3 eV probe pulses. An unoccupied interface state lying 0.3 eV above the Fermi energy arises at the TiOPc/Ag(111) interface. Although a second TiOPc layer is used to form the organic heterostructure and separate the PTCDA from the silver, we observe a resonant enhancement of the interface state for 2.3 eV pump photons, which corresponds to the excitonic HOMO-LUMO transition in PTCDA. We find a time delayed transfer of electrons from PTCDA across the TiOPc layers into the interface state on the time scale of approximately 200 fs. Our results indicate the importance of the interface state for charge carrier dynamics at heterostructures close to the Ag(111) surface.

O 85.8 Thu 17:00 S051

Nanoscale Imaging of Charge Carrier and Exciton Trapping at Structural Defects in C₆₀ Films — ●CHRISTOPH GROSSE¹, OLLE GUNNARSSON¹, PABLO MERINO¹, KLAUS KUNKE¹, and KLAUS KERN^{1,2} — ¹Max-Planck-Institut für Festkörperforschung, Heisenbergstraße 1, 70569 Stuttgart, Germany — ²École Polytechnique Fédérale de Lausanne, 1015 Lausanne, Switzerland

Charge carrier and exciton trapping in organic semiconductors crucially determine the performance of organic (opto-) electronic devices, such as organic field-effect transistors, light-emitting diodes, or solar cells. However, the microscopic origin of the relevant traps generally remains unclear, as most spectroscopic techniques are unable to probe the electronic structure of individual traps and the morphological structure causing them. Here, we employ low-temperature scanning tunneling microscopy (STM) and tunneling spectroscopy as well as tight-binding calculations derived from ab initio calculations to image the localized electronic states arising at structural defects in thin C₆₀ films (<10 ML). The spatially and spectrally resolved STM-induced luminescence at these states reveals an enhanced radiative decay of excitons, which is interpreted in terms of the local symmetry lowering and the trapping of excitons by an X-traps. The combined mapping of the STM-induced luminescence, electronic structure, and morphology thus provides new insights into the origin and characteristics of individual exciton traps in organic semiconductors and opens new avenues to study charge carrier and exciton dynamics at molecular scales.

O 85.9 Thu 17:15 S051

Theory of excitation transfer in hybrid inorganic/organic systems: Coulomb transfer between semiconductor and molecular layers — ●JUDITH SPECHT¹, EIKE VERDENHALVEN¹, SVERRE THEUERHOLZ¹, ANDREAS KNORR¹, MARTEN RICHTER¹, BJOERN BIENIEK², and PATRICK RINKE^{2,3} — ¹Institut für Theoretische Physik, Nichtlineare Optik und Quantenelektronik, Technische Universität Berlin, Berlin, Germany — ²Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany — ³Aalto University, Aalto, Finland

Hybrid inorganic/organic systems form a novel class of composite materials with interesting optoelectronic properties. Due to the Coulomb interaction, Wannier-exciton like states in an inorganic semiconductor nanostructure are coupled to Frenkel excitons occurring in organic

materials. The considered structure consists of a thin, highly ordered molecular film adsorbed on a semiconductor quantum well. Based on a density matrix theory, we study the Förster-type non-radiative excitation transfer across the hybrid interface. The microscopic input parameters are taken from ab initio calculations for ladder-type quaterphenyl (L4P) molecules on the ZnO(10 $\bar{1}$ 0) surface [1]. As a consequence of microscopic momentum selection rules, the coupling strength between the two constituents varies for different coverage densities of the semiconductor surface with molecules. Our findings can be used for optimizing the energy transfer efficiency by modifying the geometry of the hybrid structure.

[1] Verdenhalven et al., Phys. Rev. B **89**, 235314 (2014).

O 85.10 Thu 17:30 S051

Photo Switching the Optical Nonlinear Response of a Fulgimide Functionalized Silicon Surface — ●MARC HÄNSEL¹, CHRISTOPH BARTA², KAROLA RÜCK-BRAUN², and PETRA TEGEDER¹ — ¹Physikalisch-Chemisches Institut, Universität Heidelberg, Germany — ²Institut für Chemie, Technische Universität Berlin, Germany

Fulgimides are a group of molecules which undergo a ring closing and opening reaction under illumination with UV and visible light. They can retain their photochromic properties after binding to a silicon surface by a well-chosen linker molecule. Due to the large hyperpolarizability of the molecules the nonlinear optical (NLO) properties of the surface can be controlled by illumination with light. The samples were investigated with second harmonic generation (SHG), taking advantage of the symmetry of the substrate, which generates no SHG signal. We will show that a controlled photoinduced reversible change of the NLO properties of an indolylfulgimide functionalized silicon surface is possible.

O 85.11 Thu 17:45 S051

Reversible photo-switching of spiropyran molecules in direct contact with a single crystal — ●FABIAN NICKEL, MATTHIAS BERNIEN, KAI KRAFFERT, DENNIS KRÜGER, LUCAS M. ARRUDA, LALMINTHANG KIPGEN, and WOLFGANG KUCH — Institut für Experimentalphysik, Freie Universität Berlin, 14195 Berlin, Germany

The photochromic isomerization of molecules in direct contact with solid surfaces plays an important role for the further miniaturization of electronic devices. A good candidate for this purpose is spiropyran (SP). SP can be switched from a closed form to an open form (merocyanine, MC) by UV light and reversibly back by visible light. In nitro-spiropyran, however, the backreaction was found to be quenched on surfaces [1]. The modification of the end group from nitro- to naphtho-spiropyran leads to a lower electric dipole moment in the open form, which might favor switching back to the open form on a surface. In-situ x-ray absorption fine structure (NEXAFS) measurements at the nitrogen and oxygen edges prove and quantify the photoisomerization of these molecules on a Bi(111) surface. Illumination by UV light leads to an efficient switching to the open MC form of the molecule and, furthermore, a determination of the energy barriers of the photo-excited and metastable states becomes possible by temperature-dependent measurements. Visible light triggers the relaxation back to the closed SP form, thus offering full reversible control of the isomerization in direct contact with a single crystal surface.

This work is supported by the DFG through Sfb 658.

[1] Piantek et al. J. Am. Chem. Soc. **131**, 12729 (2009).