

CPP 53: Inorganic/organic interfaces: Electronic properties II (joint session O, CPP)

Time: Wednesday 15:00–18:15

Location: HE 101

Invited Talk

CPP 53.1 Wed 15:00 HE 101

Electronic structure of Organo-Metal Halide Perovskites Films and Interfaces — ●ANTOINE KAHN — Princeton University, Princeton, NJ, USA

This talk reviews direct and inverse photoemission data on the electronic structure of organo-metal halide perovskites, i.e., methylammonium lead tri-halides (MAPbX, X=Br, I, I₃-xCl_x), and of their interfaces with hole- and electron-transport layers (HTL, ETL). Valence and conduction band edges of the MAPbX films, ionization energy and electron affinity (IE, EA) are determined [1]. Good alignment of the MAPbX conduction band minimum with that of the electron-collecting oxide is found, suggesting minimal energy loss during electron extraction at this interface. The hole-extraction interface is investigated for several HTLs. Results clearly put into evidence the role of interface energetics in terms of carrier loss-less extraction or confinement in the perovskite layer [2]. The electronic structure of the inverted solar cell, with MAPbI₃ on sol-gel processed NiO_x, is also investigated [3]. The perovskite takes on a p-type character, indicative of a low density of deep gap states in the material. The NiO_x/MAPbI₃ interface energetics provide barrier-free hole extraction (0.2 eV energy loss) and a high electron-blocking barrier. On the other side of the cell, C60 and derivatives form adequate ETLs, with neither a barrier for electron extraction nor a loss in accessible open circuit voltage.

[1] P. Schulz et al., *Energ. & Envir. Sci.* 7, 1377 (2014) [2] E. Edri et al., *J. Phys. Chem. Lett.*, 5, 429 (2014) [3] P. Schulz et al. (under review)

CPP 53.2 Wed 15:30 HE 101

Site-specific transport levels in a crystalline organic thin film — ●TOMOKI SUEYOSHI, MARTIN WILLENBOCKEL, SERGUEI SOUBATCH, and STEFAN TAUTZ — Peter Grünberg Institut (PGI-3), JARA, Forschungszentrum Jülich, Germany

Recent studies have revealed that the electronic properties of organic semiconductor thin films are not only determined by the nature of individual constituent molecules, but also correlated with geometric structure in which the molecules arrange. If a crystalline organic thin film consisting of single-component molecules contains several different molecular species in its unit cell, molecular orbital energies of such species could be different from species to species depending on their relative geometry and orientation. Since it is the highest occupied/lowest unoccupied molecular orbitals (HOMO/LUMO) which are involved in charge transport, the energy dispersity of these transport levels may dominate the transport properties of organic semiconductors.

A previous scanning tunneling spectroscopy study revealed that a LUMO energy dispersity up to 0.5 eV originates from the intermolecular polarization/interaction on the LUMO of six different tetracene species in the complex bilayer β -phase on Ag(111). To access the one on the HOMO, we have performed photoelectron spectroscopy of the tetracene β -phase and observed a similar energy dispersity of the HOMO. In this talk, we will discuss the assignment of the observed HOMO components and provide a comprehensive picture of the transport levels of the tetracene β -phase.

CPP 53.3 Wed 15:45 HE 101

Charge Transport through Molecular Monolayers: Impact of Collective Effects and Docking Groups — ●VERONIKA OBERSTEINER¹, DAVID EGGER^{1,2}, GEORG HEIMEL³, and EGBERT ZOJER¹ — ¹Institute of Solid State Physics, NAWI Graz, Graz University of Technology, Graz, Austria. — ²Department of Materials and Interfaces, Weizmann Institute of Science, Rehovoth, Israel. — ³Institut für Physik, Humboldt-Universität zu Berlin, Berlin, Germany.

For advancing the exciting field of molecular electronics, a microscopic understanding of charge transport through molecule-based systems is essential. Over the past years, the fundamental physical differences between devices comprising an individual molecule or a homogeneous monolayer have been increasingly acknowledged. Here, we relate those differences to collective electrostatic effects arising from the combined electric fields of all molecules within a monolayer. Employing density functional theory in conjunction with a Green's function approach, we theoretically investigate current-voltage characteristics of metal-molecule-metal systems that comprise either single molecules or an assembly. We show that, depending on the chemical nature of the molec-

ular backbones and the used docking groups, collective effects either significantly increase or decrease the current at a given voltage. As a consequence, the 'ideal' docking group is clearly different for monolayer and single-molecule devices. These insights are also used to design molecules in which collective effects cancel, and thus transport characteristics remain largely unaffected by environmental effects.

CPP 53.4 Wed 16:00 HE 101

Inverse electron transfer in nitro-substituted monomolecular films — PRASHANT WASKE^{1,2}, ●TOBIAS WÄCHTER¹, ANDREAS TERFORT², and MICHAEL ZHARNIKOV¹ — ¹Applied Physical Chemistry, Heidelberg University, 69120 Heidelberg, Germany — ²Institut für Anorganische und Analytische Chemie, Universität Frankfurt, 60438 Frankfurt, Germany

Self-assembled monolayers of nitro-substituted aromatic thiols were prepared on Au(111) substrates and characterized by several complementary spectroscopic techniques. The introduction of the nitro tail group had a positive effect on the quality of the monolayers, which were either superior or comparable to their non-substituted analogues. All molecules in the films were found to be bound to the substrate via the thiolate anchor and to have an upright orientation. The [N 1s] π^* and [O 1s] π^* decay spectra of the monolayers did not exhibit any trace of charge (electron) transfer (CT) through the molecular framework to the substrate, following the resonant excitation of the tail group. This was explained by the energy considerations hindering CT to the substrate but enabling a reverse process (ICT), i.e. the neutralization of the core ionized state by electron transfer from the substrate/molecular backbone. Traces of this process could be tentatively identified as an admixture of resonant contributions to the non-resonant decay spectra at the O K-edge. The experimental data suggest that only the ring adjacent to the nitro group was involved in the ICT process.

CPP 53.5 Wed 16:15 HE 101

Probing single donor-acceptor molecules on thin insulating films — ●TOBIAS MEIER¹, RÉMY PAWLAK¹, SHIGEKI KAWAI¹, SHI-XIA LIU², SILVIO DECURTINS², ERNST MEYER¹, and THILO GLATZEL¹ — ¹Department of Physics, University of Basel, Switzerland — ²Department of Chemistry and Biochemistry, University of Bern, Switzerland

Fused Donor-Acceptor molecules have attracted a broad interest due to their potential applications for example in organic solar cells. The intrinsic electronic properties of such organic compounds determine the device performance, notably the intramolecular charge transfers (CT) between the donor and acceptor parts. However, the CT is still poorly understood at the single molecular scale.

In this work we used the TTF-dppz [1], a planar and π -conjugated molecule with size of less than 2 nm, adsorbed on thin layers of NaCl on Cu(111). By combining STM and AFM, we spatially characterized the separation of the HOMO and LUMO with respect to the chemical structure of the TTF-dppz molecule observed by AFM. We further investigated with force and current based spectroscopic techniques [2,3] the electronic properties of the molecule and its charge redistribution. To gain more insights into the charge transfer of a single molecule under illumination, we further performed such spectroscopic measurements under illumination.

[1] C. Jia et al., *Chemistry* 13, 3804 (2007). [2] R. Pawlak et al., *Nano Lett.* 13, 5803 (2013). [3] S. Kawai et al., *ACS Nano* 7, 9098 (2013).

CPP 53.6 Wed 16:30 HE 101

Integer versus fractional charge transfer at metal/organic and metal/insulator/organic interfaces: Cu(/NaCl)/TCNE — ●OLIVER T. HOFMANN^{1,2}, PATRICK RINKE^{1,3}, VIKTOR ATALLA¹, GEORG HEIMEL⁴, and MATTHIAS SCHEFFLER¹ — ¹FHI Berlin, Germany — ²TU Graz, Austria — ³Aalto University, Helsinki, Finland — ⁴Humboldt University Berlin, Germany

We use semilocal and hybrid density functional theory to study the charge transfer and level alignment at a representative interface between a metal and an organic molecule. To reduce the hybridization strength between the adsorbate and the substrate, we also insert thin insulating NaCl buffer layers. We find that upon direct adsorption on the metal, charge is perfectly delocalized across all molecules, lead-

ing to a laterally homogenous layer. However, when the hybridization between metal and organic is prevented by an insulating interlayer, charge localizes on individual moieties, creating laterally inhomogeneous charge distributions. This spontaneous breaking of the translation symmetry is reflected in several observables, such as the molecular geometry or the valence and core densities of states. We find that the amount of charge transfer is determined, to a significant extent, by the ratio of the lateral spacing of the molecules and their energetic distance to the electron reservoir, i.e., the metal. Therefore, the amount of charge transfer does not only depend on the electronic structure of the individual components, but also on the interface geometry. Furthermore, we discuss the impact of the lateral charge distribution on the coverage dependence of the work function for different growth models.

CPP 53.7 Wed 16:45 HE 101

Controlled photo-induced work function manipulation of the TCNQ/Au(111) interface — ●DAVID GERBERT and PETRA TEGEDER — Physikalisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg, Germany

One of the most important tasks to improve the performance of organic electronic devices is the development of deeper understanding and purposeful employment of metal electrode*s work function manipulation [1]. In the first layer TCNQ is known to be negatively charged on various metal surfaces [2,3], however only on Au(111) it is neutral [4]. We investigated the electronic structure of the TCNQ/Au(111) interface by means of two-photon-photoemission (2PPE) and observed a photo-induced work function shift of several hundred meV, which points towards photo-induced electron transfer from the gold substrate to the molecule. Interestingly the work function can be continuously tuned across the clean surface value which establishes new application possibilities of TCNQ as device-adapted hole-injection layer.

[1] N. Koch, ChemPhysChem. 8, 1438-1455 (2007).

[2] C. Park et al., Phys. Rev. B 90, 125432 (2014).

[3] T.-C. Tseng et al., Nat. Chem. 2, 374 (2010).

[4] I. Fernandez-Torrente et al., Int. J. Mass Spectrom. 277, 269-273 (2008).

CPP 53.8 Wed 17:00 HE 101

The geometric and electronic structure of TCNQ and TCNQ+Mn on Ag(001) surface — VITALY FEYER¹, MARTIN GRAUS^{2,3}, ●GIOVANNI ZAMBORLINI¹, ROBERT G. ACRES⁴, ACHIM SCHÖLL^{2,3}, FRIEDRICH REINERT^{2,3}, and CLAUD M. SCHNEIDER^{1,5} — ¹Research Center Jülich, 52425 Jülich, Germany — ²Universität Würzburg, Experimentelle Physik VII & Röntgen Research Center for Complex Material Systems RCCM, 97074 Würzburg, Germany — ³Karlsruher Institut für Technologie KIT, Gemeinschaftslabor für Nanoanalytik, 76021 Karlsruhe, Germany — ⁴Sincrotrone Trieste, 34012 Basovizza, Trieste, Italy — ⁵Universität Duisburg-Essen, D-47048 Duisburg, Germany

We have investigated the geometric and electronic structure of ordered monolayers of TCNQ and of TCNQ+Mn on Ag(001) surface by LEED and photoelectron momentum microscopy (at the NanoESCA beamline of the Elettra synchrotron). Two coverage dependent, commensurate superstructures are established on Ag(001) while the co-adsorption of Mn results in the formation of a long-range ordered mixed metal-organic superstructure, which is also commensurate. From ARPES pattern of the TCNQ LUMO the azimuthal orientation of the molecules in the respective unit cell can be determined. The PES data shows, in the case of TCNQ/Ag(100) a filling of the TCNQ LUMO by charge transfer from the substrate while the coadsorption of Mn leads to an energy shift of the TCNQ HOMO and LUMO of 230 meV with respect to TCNQ/Ag(001). No significant lateral band dispersion in the adsorbate layers was observed in ARPES data.

CPP 53.9 Wed 17:15 HE 101

Adsorption and electronic properties of tetraazaperopyrene derivatives on Au(111) — ●FRIEDRICH MAASS¹, STEPHAN STREMLAU¹, LENA HAHN², LUTZ H. GADE², and PETRA TEGEDER¹ — ¹Physikalisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg, 69120 Heidelberg, Germany — ²Anorganisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg, 69120 Heidelberg, Germany

The adsorption behavior of large N-heterocyclic pi-conjugated molecules is of immense interest for understanding the structural and electronic properties of this new class of organic n-channel semiconductors.

We investigated the adsorption geometry and the electronic

properties of 1,3,8,10-tetraazaperopyrene (TAPP) and its 2,9-bis(perfluoroalkyl)-4,7,11,14-tetra-X derivatives (X is H, Cl, Br or I) on the Au(111) surface with vibrational and electronic high resolution electron energy loss spectroscopy (HREELS) and thermal desorption spectroscopy (TDS). We found a different adsorption behavior between substituted and unsubstituted TAPP and also between monolayer and corresponding multilayers. HOMO-LUMO gaps have been investigated by electronic HREEL spectroscopy and are in good agreement with previously made UV/VIS and calculated data.

CPP 53.10 Wed 17:30 HE 101

Effects of embedded dipole in alkanethiolate self-assembled monolayers — SWEN SCHUSTER¹, NICHOLE SULLIVAN², ORLANDO CABARCOS², IRIS HEHN³, JEAN-FRANÇOIS MORIN⁴, EGBERT ZOJER³, DAVID L. ALLARA², and ●MICHAEL ZHARNIKOV¹ — ¹Angewandte Physikalische Chemie, Universität Heidelberg, 69120 Heidelberg, Germany — ²Department of Chemistry, Pennsylvania State University, University Park, PA 16802, USA — ³Institute of Solid State Physics, Graz University of Technology, 8010 Graz, Austria — ⁴Département de chimie, Faculté des sciences et de génie, Université Laval, Québec QC G1V 0A6, Canada

Self-assembled monolayers (SAMs) bonded to metal electrodes are capable to improve charge-carrier injection across the metal-organic interface. This is usually achieved by use of the terminal dipolar groups (terminal dipole) comprising the outer interface of SAMs. But such an architecture affects the growth mode of an organic semiconductor (in the standard device configuration) entangling it with the dipole control. In contrast, for the molecules with an embedded dipolar element, the dipole control and the chemistry at the SAM-ambient interface are decoupled. In this context, we studied a series of SAMs prepared on Au{111} from the mid-chain ester functionalized alkanethiols. The presence of the ester moiety leads to interesting electrostatic effects in photoemission and allows to modify the work function of the substrate in a certain range. The results are rationalized with a help of theoretical simulations, involving a combination of DFT and molecular dynamics methods.

CPP 53.11 Wed 17:45 HE 101

The Role of Pauli-Pushback for the Electronic Properties of Self-Assembled Monolayers at Reduced Coverage — ●ELISABETH VERWÜSTER¹, DAVID A. EGGER^{1,2}, OLIVER T. HOFMANN¹, and EGBERT ZOJER¹ — ¹Institute of Solid State Physics, Graz University of Technology, NAWI Graz, Petersgasse 16, 8010 Graz, Austria — ²Department of Materials and Interfaces, Weizmann Institute of Science, Rehovoth 76100, Israel

Using density-functional theory, advanced geometry optimization tools and accounting for van der Waals interactions we explain the coverage-dependent electronic structure of self-assembled monolayers (SAMs). As model systems for our calculations we choose acceptor- (-CN, -CF₃) and donor- (-CH₃, -NH₂) substituted biphenylthiols on a Au(111) surface. Our focus lies on changes in the SAM-induced work-function modification, $\Delta\Phi$. Upon reducing the coverage the tilt angle of the molecules strongly increases. The latter significantly affects the molecular dipole perpendicular to the surface. The resulting changes in $\Delta\Phi$ are, however, much more pronounced than one could expect on purely geometric grounds. For example, $\Delta\Phi$ vanishes already at a coverage of 50% for the acceptor-substituted SAMs. This can only partly be explained by the tilt-angle dependence of the charge-rearrangements arising from the S-Au bond formation. Instead, we show that especially at low coverage the interaction-induced charge-rearrangements at the interface are dominated by Pauli-pushback, an effect well known for flat-lying adsorbates.

CPP 53.12 Wed 18:00 HE 101

Electrostatic design of monolayer properties — BERNHARD KRETZ¹, DAVID A. EGGER^{1,2}, and ●EGBERT ZOJER¹ — ¹Institute of Solid State Physics, NAWI Graz, Graz University of Technology, Petersgasse 16, A-8010 Graz, Austria — ²Department of Materials and Interfaces, Weizmann Institute of Science, Rehovoth 76100, Israel

For raising the full potential of molecular electronics, it is necessary to control the nature of the electronic states within organic layers. In this contribution we present the concept of a modular toolbox that allows realizing a high level of control as far as the energetics and spatial localization of the states is concerned. By quantum-mechanical modelling we show that - based on this toolbox - it is, for example, possible to realize monolayer-based quantum-cascades and electron or hole quantum-well structures. This becomes possible by exploiting

collective electrostatic effects naturally emerging in ensembles of polar molecules. As another element of the toolbox we discuss neutral

radicals that can be applied for generating locally spin-polarized layers.