

DS 16: Organic Thin Films, Organic-Inorganic Interfaces

Time: Wednesday 9:30–12:30

Location: H39

DS 16.1 Wed 9:30 H39

Visualising the Vertical Energetic Landscape in Organic Photovoltaics — •VINCENT LAMI¹, ANDREAS WEU¹, JIANGBIN ZHANG², YONGSHENG CHEN³, ZHUPING FEI⁴, MARTIN HEENEY⁴, RICHARD FRIEND², and YANA VAYNZOF¹ — ¹KIP/CAM, Heidelberg University, GER — ²Cavendish Laboratory, University of Cambridge, UK — ³Nankai University, Tianjin, China — ⁴Chemistry & CPE, Imperial College London, UK

Energy level diagrams in organic photovoltaic (OPV) devices play a crucial role in interpretation of device physics, since they determine elementary processes such as charge generation, transport or extraction. Despite the importance of these diagrams, they are currently often constructed by combining energetic values of the individual device components, without taking into account interfacial effects, such as band bending or dipole formation. Herein, we demonstrate that combining ultra-violet photoemission spectroscopy (UPS) with gas cluster ion beam sputtering allows for a damage-free depth profiling and hence, an accurate determination of the vertical energetic landscape of active layers. First, we utilize a model photovoltaic system, then we demonstrate our method on other high efficiency fullerene and non-fullerene systems. We are not only able to accurately measure the highest occupied molecular orbital (HOMO) offset of the contributing materials and to quantify energy losses, but also to obtain compositional information with a very high vertical depth resolution. Finally, as UPS depth profiling can be performed at any point in device lifetime, it offers valuable information after device operation or degradation.

DS 16.2 Wed 9:45 H39

Titanylphthalocyanine Films on Ag(111): an Epitaxial Metal/Organic Hetero-System with Exceptional Smooth Surface — •MICHAEL KOTHE, FELIX WIDDASCHECK, and GREGOR WITTE — Philipps-Universität, Marburg, Germany

The chemical and thermal robustness of titanyl-phthalocyanine (TiOPc) in combination with its high optical absorption favours its application as photoconductor or chromophore for light-harvesting in organic photovoltaic applications. Beside such device application there is a large interest in the controlled fabrication of smooth molecular spacer layers of controlled thickness in order to prepare molecular heterostructures. While many pi-conjugated materials form highly ordered mono- and bilayer films on metallic (single crystalline) substrates, the films exhibit a notable roughness upon increasing film thickness. Here, we demonstrate that TiOPc forms extremely smooth films on Ag(111), not only in the mono- and bilayer regime but also for films exceeding a thickness of 10nm. Combining various techniques including atomic force and scanning tunnelling microscopy (AFM, STM), with X-ray photoelectron spectroscopy (XPS), near-edge X-ray absorption fine structure spectroscopy (NEXAFS) and X-ray diffraction (XRD), we show that for substrate temperatures below 450 K TiOPc forms molecularly smooth films with a small overall film roughness. The analysis shows that the films are stabilized by molecular bilayers of alternately (up and down) oriented titanyl. Finally, we show that even the thick films are epitaxially oriented with respect to the azimuth direction of the Ag(111) surface.

DS 16.3 Wed 10:00 H39

Vacuum-deposited organic monolayers for work function modification of noble metal electrodes — •FELIX WIDDASCHECK, ALRUN ALINE HAUKE, and GREGOR WITTE — Molekulare Festkörperphysik, Philipps-Universität Marburg, D-35032 Marburg, Germany

The energy level alignment between organic semiconductors and the respective (metal) electrodes in organic electronic devices is of key importance for efficient charge carrier injection. For many years, researchers have attempted to control this energy level alignment by means of functional self-assembled monolayers (SAMs) or the insertion of thin injection layers (made e.g. of doped organic semiconductors or pure dopants). The present work demonstrates an alternative approach, namely the use of phthalocyanine monolayers as contact primers which are deposited onto noble metal electrodes by means of vacuum deposition. We show that polar as well as non-polar phthalocyanines modify the work functions of clean Au(111) and Ag(111) surfaces as a function of their coverage and thus enable quantitative control of the metal work functions. This behavior is successfully replicated for polycrys-

talline metal surfaces and it is found that full monolayers can even withstand air exposure when protected by sacrificial multilayers which are afterwards removed by thermal desorption.

DS 16.4 Wed 10:15 H39

Thermal emission from a hybrid plasmonic structure in the strong coupling regime — •HALA MEMMI, OLIVER BENSON, SERGEY SADOFEV, and SASCHA KALUSNIAK — Institut für Physik, Humboldt Universität zu Berlin, Berlin, Germany

We report on thermal emission from an organic/inorganic plasmonic hybrid structure where a carbonyl stretching vibration is strongly coupled with a surface plasmon polariton. The structure consists of a polyvinyl-methyl-ketone layer deposited on top of a silver layer. Emission measurements in Kretschmann-Raether configuration using a calcium fluoride hemicylindrical prism as decoupling medium were conducted at 140°C and collected in transverse magnetic polarization. Two clear maxima corresponding to upper and lower polariton branch were observed in the emission spectra. They also reproduce the anti-crossing behavior in the dispersion relation as revealed from Attenuated-total-reflection measurements. The intensity of the emission maxima as a function of the varying temperature confirms the different nature of the branches.

DS 16.5 Wed 10:30 H39

Reaction of Calcium with Tetraphenylporphyrin Thin Films: Reaction Energies and Reaction Depths — •MAIK SCHÖNIGER, STEFAN RENATO KACHEL, CLAUDIO K. KRUG, TABEA KOEHLER, MARTIN SCHMID, and J. MICHAEL GOTTFRIED — Philipps-Universität Marburg, Fachbereich Chemie, Hans-Meerwein-Str. 4, 35032 Marburg

We have investigated the interface reaction of vapour-deposited calcium (Ca) with tetraphenylporphyrin (2HTPP) thin films (20-30 nm) by means of Hard X-Ray Photoemission Spectroscopy (HAXPES) and Nanojoule Adsorption Calorimetry (NAC). The importance of low work-function materials and organic semiconductors is obvious as they are commonly used in organic electronics. However, their interfacial interactions are poorly understood. Clarifying diffusion and reaction processes occurring during metal deposition onto the organic material is crucial for a deeper understanding of the performance of such systems. The Ca/2HTPP system is a model system that allows us to study the energetics of a typical interface reaction and to establish concentration depth profiles of the resulting interphase layer, which here consists of the reaction product CaTPP. Using HAXPES, we measured depth profiles of the interface region for different preparation conditions of the interface. Parameters such as temperature or flux of the Ca atoms were varied. As complementary data, we will report enthalpies of adsorption and reaction, measured using NAC coupled with a pulsed Ca atomic beam source. The apparatus allows the direct measurement of these quantities, which cannot be obtained by temperature-programmed desorption or similar frequently used methods.

DS 16.6 Wed 10:45 H39

Measuring and Modelling Electric Potential Distributions at Organic Semiconductor Interfaces — •MARKUS FRERICKS^{1,2}, CHRISTOF PFLUMM³, WOLFRAM JAEGERMANN^{1,2}, and ERIC MANKEL^{1,2} — ¹Technische Universität Darmstadt, Darmstadt — ²InnovationLab, Heidelberg — ³Merck KGaA, Darmstadt

Photoelectron spectroscopy (PES) is an important characterization method in the field of semiconductor physics. Consecutive deposition of thin layers of an adsorbate on a substrate monitored by PES allows for an analysis of the electronic structure at semiconductor interfaces. For organic semiconductors (OSCs), several publications, e.g. [1], indicate that the key to understand contact formation and doping mechanisms lies in the disorder of organic molecules and its influence on the density of states (DOS). Supporting this idea, we developed a model based on the ones presented by Salzmann et. al. and Lange et. al. [1,2] to numerically calculate the potential distribution at OSC interfaces. Combining these calculations with the approach of Ohashi et. al. [3] to simulate PES data, we derived an algorithm to fit the results of above-mentioned type of interface experiment. By this means, we obtained a tool that supports the importance of the DOS and allows for further investigations on its influence and behavior at contacts. After

presenting the procedure, we will demonstrate its applicability on the results of interface experiments with differently doped hole transport materials.

[1] Salzmann et. al., *Acc. Chem. Res.* 49 (2016) [2] Lange et. al., *PRL* 106 (2011) [3] Ohashi et. al., *Appl. Phys. Lett.* 101 (2012)

15 min. break.

DS 16.7 Wed 11:15 H39

Semi-transparent organic detectors for standing wave sensing applications — ●VLADISLAV JOVANOVIĆ¹, PATRICE DONFACK¹, ARNE MÜLLER¹, ARNULF MATERNY¹, DIETMAR KNIPP², and VEIT WAGNER¹ — ¹Jacobs University Bremen, 28759 Bremen, Germany — ²Stanford University, Stanford, CA 94305, USA

Organic semiconductor materials are widely used for the development and realization of optoelectronic devices because of their compatibility with solution processing fabrication and printing techniques. Currently, light emitting diodes and solar cells are the most developed areas of application of organic materials. The huge potential of organic materials is still not fully explored in other application areas among which optical sensing and spectrometers could be very promising. In this investigation, a fast and compact standing wave spectrometer based on semi-transparent organic photodetectors is developed [1]. The semi-transparent organic detectors are realized using polymer-fullerene material systems and solution-based fabrication. The fabricated semi-transparent detectors exhibit an overall transmittance of about 20% in the visible range of the electromagnetic spectrum. The realization of a standing wave spectrometers is achieved by combining fabricated semi-transparent organic detectors with a movable mirror controlled by a piezo micro-actuator. The unique advantages of standing wave sensing devices based on organic materials as well as the required material properties are presented and discussed.

[1] V. Jovanov, P. Donfack, A. Müller, A. Materny, D. Knipp, and V. Wagner, *J. Mater. Chem. C* 6, 11457-11464 (2018).

DS 16.8 Wed 11:30 H39

Pentacene and Perfluoropentacene Bilayers – Well-Defined Interfaces vs. Molecular Intermixture — ●PIERRE DOMBROWSKI, TOBIAS BREUER, STEFAN RENATO KACHEL, J. MICHAEL GOTTFRIED, and GREGOR WITTE — Philipps-Universität Marburg, Germany

Precisely studying organic donor/acceptor systems is crucial for the improved understanding and design of organic optoelectronic devices. Heterostructures of p-type organic semiconductors (OSCs) and fluorinated n-type OSCs are particularly attractive donor/acceptor systems as they tend to form H-F bonds that favor the formation of intermixed supramolecular assemblies. Within these, pentacene (PEN) and perfluoropentacene (PFP) are an interesting model system due to their structural compatibility. The present study combines near-edge X-ray absorption fine structure (NEXAFS), temperature programmed desorption (TPD) and scanning tunneling microscopy (STM) measurements to characterize the intermixture of PEN and PFP on molybdenum disulfide as well as the Ag(111) and Au(111) surfaces. NEXAFS spectra of PEN and PFP bilayers show that it is possible to prepare nicely ordered bilayers without mutual intermixing. Only upon annealing, molecular intermixture is activated. TPD measurements reveal an attractive intermolecular interaction in the heterostructure, in contrast to repulsive interaction in the unitary phases, and suggest the formation of a thermally stabilized 1:1 intermixture, in line with previous TPD results [1]. STM images directly show intermixed phases that support the model of a stabilization by H-F bonds.

[1] T. Breuer and G. Witte, *J. Chem. Phys.* (2013), 138, 114901

DS 16.9 Wed 11:45 H39

Low-Dimensional Hybrid Interfaces Between Acenes and TMDCs: Pentacene and Perfluoropentacene on MoS₂ — ●STEFAN RENATO KACHEL, PIERRE DOMBROWSKI, TOBIAS BREUER, GREGOR WITTE, and J. MICHAEL GOTTFRIED — Philipps-Universität Marburg, Germany

Pentacene (PEN) is a widely investigated organic semiconductor used

for fabrication of thin film transistors. Upon fluorination, the electronic configuration of perfluoropentacene (PFP) undergoes drastic changes that influence its adsorption and growth behavior. The differences of PEN and PFP have been studied on bulk as well as on 2D layered MoS₂ by multiple techniques such as near-edge X-ray absorption fine structure (NEXAFS), X-ray photoelectron spectroscopy (XPS), temperature-programmed desorption (TPD) and optical spectroscopy. In NEXAFS, we found flat-laying monolayers of PEN and PFP on both bulk and 2D layers MoS₂. TPD shows a distinct monolayer peak characterized by a typical peak broadening and a peak maximum shift to lower temperatures as often found for organic adsorbates. Moreover, PFP submonolayers desorb at 30 K higher temperatures than PEN giving evidence for a higher binding energy to the substrate. The multilayer desorption is in agreement with other studies. Gentle heating allows the reliable desorption of the multilayers while leaving a well-defined monolayer behind, both on bulk as well as 2D-MoS₂. This preparation gives rise to further spectroscopic methods allowing the examination of the electronic properties of a perfectly defined interface between precisely one OSC layer and a 2D-TMDC substrate.

DS 16.10 Wed 12:00 H39

Multi-analytical investigation of tetrapodal self-assembled monolayers on gold: Formation and Functionality — ●VALENTINA ROHNACHER^{1,2}, FRANK SIMON BENNECKENDORF^{2,3}, MAYBRIT MÜNCH^{2,4}, SEBASTIAN BECK^{1,2}, and ANNEMARIE PUCCI^{1,2} — ¹Kirchhoff Institute for Physics, Uni Heidelberg — ²Innovationlab, Heidelberg — ³Institute of Organic Chemistry, Uni Heidelberg — ⁴Surface Science Division, TU Darmstadt

Self-assembled monolayer (SAMs) have proven to form stable and well-defined layers on various electrode materials increasing the interfacial compatibility in organic electronic devices.[1,2] A novel tetrapodal SAM molecule with four thiol-anchor groups was synthesized which enables fourfold binding to the gold substrate, enforcing a perpendicular orientation of the molecular dipole relative to the metal surface. We perform infrared reflection-absorption spectroscopy (IRRAS) measurements on tetrapodal diazaitycene molecules on evaporated gold substrates to probe the orientation and quality of the SAMs. In comparison with contact angle measurement and photoelectron spectroscopy, a better understanding about the SAM formation and electrode modification was achieved.

[1] Jesper et al. *Langmuir* 2015, 31, 37, 10303-10309

[2] Benneckendorf et al. *J. Phys. Chem. Lett.* 2018, 9, 13, 3731-3737

DS 16.11 Wed 12:15 H39

Switching the surface electronic properties of polar ZnO crystals with photochromic pyridyl-dihydropyrene molecular layers — ●QIANKUN WANG¹, GIOVANNI LIGORIO¹, RAPHAEL SCHLESINGER¹, VALENTIN DIEZ-CABANES², DAVID CORNIL², YVES GARMSHAUSEN¹, STEFAN HECHT¹, JÉRÔME CORNIL², EMIL J. W. LIST-KRATOCHVIL¹, and NORBERT KOCH¹ — ¹Humboldt-Universität zu Berlin — ²University of Mons

Remote control of the electronic energy levels by external stimuli such as light will enable optoelectronic devices with improved or additional functionalities. Here, we demonstrate that the electronic properties of ZnO interfaced with molecular negative T-type photoswitches, i.e., pyridyl-dihydropyrene (Py-DHP), can indeed be photomodulated. Using photoemission spectroscopy and density functional theory (DFT) modelling, we show that the photochromic ring closure/opening process results in reversible shift of the frontier occupied molecular level by 0.7 eV with respect to the Fermi level. Notably, in both molecular configurations, the energy level alignment at the ZnO/Py-DHP interface is governed by a Fermi level pinning of the lowest unoccupied molecular level. Moreover, upon switching, we observe an increase in the ionization energy for Py-DHP multilayers compared to that of a monolayer. We attribute this to a different preferred molecular orientation in monolayer versus multilayer films. Our results show that dynamic tuning of the interface energy level alignment at inorganic/organic junctions by external stimuli is indeed possible and will aid the development of photoprogrammable opto-electronic devices.