

O 5: Organic-Inorganic Hybrid Systems and Organic Films I

Time: Monday 10:30–13:00

Location: WIL A317

O 5.1 Mon 10:30 WIL A317

The Impact of Doping on the Interface Structure and Level Alignment of ZnO/F6TCNNQ Interfaces from First Principles — ●SIMON ERKER and OLIVER T. HOFMANN — Institute of Solid State Physics, NAWI Graz, Graz University of Technology, Austria

In inorganic/organic heterostructures the interface decisively determines the performance of a device. However, in particular for materials such as ZnO, which is commonly employed in organic electronics, the surface composition is often not well known. Indeed, experimentally the polar (000-1) surface shows a wide variety of different structures, even under notionally similar conditions. Recent work indicates that doping, that is often not systematically controlled, may be responsible for the observed diversity. However, so far a theoretical verification was impeded by the lack of a computational first-principles approach that allows dealing with long-ranged band bending and charged surfaces. We present an extension of the recently introduced charged-reservoir electronic sheet technique (CREST) [PRB 91, 075311 (2015)] to incorporate band-bending effects directly into our calculations. Using DFT in combination with ab-initio thermodynamics we determine a doping dependent surface phase diagram of O-terminated ZnO. We find that the surface preferably adsorbs hydrogen to achieve a stable surface, but that its coverage becomes smaller with increasing doping concentration. We proceed to show how the different surface terminations and the corresponding band-bending affects the level alignment and the adsorption energy for the deposition of the strong electron acceptor F6TCNNQ.

O 5.2 Mon 10:45 WIL A317

Extended Space Charge Region and Unoccupied Molecular Band Formation in Epitaxial F4TCNQ Films — ●DAVID GERBERT and PETRA TEGEDER — Physikalisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg, Germany

The generation of well-defined molecular structures at inorganic/organic interfaces and within thin molecular films is crucial for charge carrier transport and thus the performance of organic-molecule-based (opto)electronic devices. In this talk we show by means of low-energy electron diffraction that F4TCNQ grows in an epitaxial fashion on Au(111) surfaces. These well-ordered crystalline films feature an extended space charge region and a dispersing unoccupied electronic molecular state as it was demonstrated using energy- and angle-resolved two-photon photoemission. The latter finding is a clear proof for band formation in epitaxial grown F4TCNQ films on Au(111). From our perspective the high electron affinity of F4TCNQ and a band-like charge transport from the interface into the molecular film are responsible for the formation of the space charge region. Our presented results suggest the application of epitaxial F4TCNQ films as hole injection layer to manipulate the hole injection barrier in organic electronic devices in a controlled way via the F4TCNQ layer thickness.

O 5.3 Mon 11:00 WIL A317

Photoemission Tomography of NiTPP on Cu(100) — ●DANIEL LÜFTNER¹, GIOVANNI ZAMBORLINI², ZHIJING FENG³, CARLO DRI³, VITALY FEYER², and PETER PUSCHNIG¹ — ¹Institut für Physik, Universität Graz, 8010, Graz, Austria — ²Peter Grünberg Institut (PGI-6), Forschungszentrum Jülich GmbH, 52425, Jülich, Germany — ³CNR-IOM Laboratorio Nazionale TASC, 34012 Trieste, Italy

In this work we present a comprehensive characterization of the geometrical and electronic structure of self assembled Nickel-tetraphenylporphyrin (NiTPP) films on Cu(100) utilizing various experimental techniques, supported by theoretical calculations using density functional theory (DFT). In particular we make use of scanning tunneling microscopy (STM), low energy electron diffraction (LEED) and photoemission tomography (PT), where the results of angle resolved photoemission spectroscopy (ARPES) measurements are systematically compared to the Fourier Transform of molecular orbitals, obtained in DFT. On the basis of STM and LEED measurements, we find, that NiTPP can arrange in two different geometrical configurations. In terms of electronic structure, PT allows for a direct assignment of peaks in the angle integrated ARPES spectrum to individual molecular orbitals and as such we observe a strong interaction of NiTPP with the metallic substrate resulting in occupation of LUMO/LUMO+1 and the LUMO+3 of the gas phase molecule. Our

work emphasizes that a multi technique approach is essential in order to have a complete picture of the adsorption behavior and electronic properties of the metal/molecule interface.

O 5.4 Mon 11:15 WIL A317

Metastable tautomers — tuning the lifetime with an STM tip — ●ANDREAS KRÖNLEIN¹, JENS KÜGEL¹, AIMEE SIXTA^{1,2}, MARKUS BÖHME¹, and MATTHIAS BODE^{1,3} — ¹Physikalisches Institut, Universität Würzburg, 97074 Würzburg, Germany — ²University of Texas at Austin, 78712 Austin, Texas, United States — ³Wilhelm Conrad Röntgen Center for Complex Material Systems (RCCM), Universität Würzburg, 97074 Würzburg, Germany

Although the influence of an scanning tunneling microscopy tip is often considered to be negligible, there are many examples where the tip is strongly affecting the physical properties of the probed system, as, for example, shown for the excitation spectra of Fe-OEP-Cl molecules [1]. Here, we present a detailed study of the tautomerization of dehydrogenated phthalocyanine molecules on a Ag(111) surface by means of scanning tunneling microscopy and STM-based pump-and-sample experiments [2]. Our data reveal that the molecule can switch between four different tautomeric forms. Whereas two of tautomers exhibit a very long lifetime, the lifetime of the other two tautomers amounts to seconds only. Current- and bias-dependent studies indicate that the presence of the STM tip modifies the potential barrier, thereby allowing for a controlled tuning of the metastable tautomer's lifetime.

[1] B. W. Heinrich *et al.*, Nature Physics **9**, 765 (2013)[2] J. Kügel *et al.*, ACS Nano in press

O 5.5 Mon 11:30 WIL A317

Breaking Degeneracy of Tautomerization - Influence of the substrate — ●MARKUS BÖHME¹, JENS KÜGEL¹, AIMEE SIXTA^{1,3}, ANDREAS KRÖNLEIN¹, and MATTHIAS BODE^{1,2} — ¹Physikalisches Institut, Experimentelle Physik II, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany — ²Wilhelm Conrad Röntgen Center for Complex Material Systems (RCCM), Universität Würzburg, Am Hubland, 97074 Würzburg, Germany — ³University of Texas at Austin, Austin, Texas 78712, United States

We present a detailed study of the tautomerization, i.e., the switching of hydrogen protons, between different sites in the molecular frame of phthalocyanine (H₂Pc) on Ag(111) by means of scanning tunneling microscopy (STM) [1]. Our data reveal that the symmetry mismatch between the substrate and the molecular frame lifts the energetic degeneracy of the two H₂Pc tautomers. Their energy difference is so large that only one tautomer can be found in the ground state. Tip-induced tautomerization was triggered at sufficiently high bias voltages. By the controlled removal of a hydrogen proton from the molecule, a four-level system was created, consisting of two stable and two metastable states .

[1] J. Kügel *et al.*, ACS Nano Article ASAP DOI: 10.1021/acsnano.6b05924

O 5.6 Mon 11:45 WIL A317

Excited states dynamics in TIPS-Pentacene on Au(111) — ●ARNULF STEIN and PETRA TEGEDER — PCI Universität Heidelberg, Heidelberg, Deutschland

Singlet fission is a promising approach to overcome the theoretical Shockley Queisser - Limit in organic semiconductor solar cells and is so far only obtained in a limited number of molecules [1]. One representative compound is the triisopropylsilylethynyl-pentacene (TIPS-Pn) which stands out because it combines solubility, self-assembly into π -stacked arrays to enhance intermolecular orbital overlap [2] and vacuum processability [3]. We studied TIPS-Pn adsorbed on Au(111) using two-photon-photoemission spectroscopy (2PPE). We determined the electronic structure and the dynamics of optically excited states at interfaces and within thin films.

[1] M.B. Smith and J. Michl, Chem. Rev. **110**, 6891 (2010)[2] J.E. Anthony *et al.*, JACS, **123**, 9482 (2001).[3] A. Gnoli *et al.* J. Phys. Chem. C, **118**, 22522 (2014).

O 5.7 Mon 12:00 WIL A317

Interaction of free-base tetraphenylporphyrin with magnesium oxide: Influence of MgO morphology on metalation

— •GIANLUCA DI FILIPPO, ANDREJ CLASSEN, REBECCA PÖSCHEL, and THOMAS FAUSTER — Lehrstuhl für Festkörperphysik, Friedrich-Alexander-Universität Erlangen-Nürnberg, Staudtstraße 7, 91058, Erlangen, Germany

Using x-ray photoemission spectroscopy we investigated the self-metalation of free-base tetraphenylporphyrin (2HTPP) on thin MgO(100) films on Ag(100). The deposition of one monolayer 2HTPP on MgO results in the formation of magnesium(II) tetraphenylporphyrin (MgTPP) at room temperature. We demonstrate that the efficiency of the reaction drastically depends on the morphology of the oxide layers. A thin MgO/Ag(100) film grown at 393 K presents a high island density [1]. Partial metalation of 1 ML 2HTPP onto this surface is already observed at a nominal MgO thickness well below 1 ML. The increase of the MgO amount leads to the progressive increase of the number of metalated molecules. Larger islands are obtained at a growth temperature of 573 K [1]. On such a substrate the metalation efficiency is consistently reduced so that partial metalation is only observed for a MgO nominal thickness above 1 ML. We ascribe these results to the fact that MgTPP formation takes place through the hydroxylation of steps and defects on the MgO surface [2], as confirmed by the increase of the OH signal in the O 1s line.

[1] A. Ouvrard *et al.*, J. Phys. Chem. C **115**, 8034 (2011)

[2] J. Schneider *et al.*, Chem. Eur. J. **22**, 1744 (2016)

O 5.8 Mon 12:15 WIL A317

Controlled On-Surface Synthesis of Organic and Organometallic Macrocycles — •QITANG FAN¹, CICI WANG², TAO WANG², JUNFA ZHU², MIN CHEN¹, MALTE ZUGERMEIER¹, CLAUDIO K. KRUG¹, JULIAN KUTTNER¹, GERHARD HILT¹, and J. MICHAEL GOTTFRIED¹ — ¹Fachbereich Chemie, Philipps-Universität Marburg, Germany — ²National Synchrotron Radiation Laboratory, University of Science and Technology of China

Macrocycles and cyclic polymers have properties distinctly different from those of their linear counterparts. While effective approaches for their synthesis in solution remain scarce, on-surface synthesis has proven to be a viable alternative due to the inherent template effects. The controlled formation of hyperbenzene and organometallic macrocycles has been achieved on metal surfaces from 4,4'-dibromo-m-terphenyl (DBMTP) precursor molecules. Hyperbenzene, a hexagon consisting of 18 phenyl rings, forms on Cu(111), Ag(111) and Au(111) with different yields, which are maximized under pseudo-high dilution conditions. On clean Cu(110), DBMTP reacts to form zigzag organometallic chains linked with C-Cu-C bonds. However, with a template based on a Cu(110)-(2 × 1)O supergrating, cyclic organometallic tetragons (MTP-Cu)₄ and hexagons (MTP-Cu)₆ are obtained on the Cu stripes (with width from 2.6 nm to 3.6 nm). These methods may pave the way for the synthesis of other macrocycles.

O 5.9 Mon 12:30 WIL A317

Electronic Properties of the Potential Organic Superconductor 1,2;8,9-Dibenzopentacene on Ag(111) — •FELIX OTTO, MAXIMILIAN SCHAAL, CHRISTIAN UDHARDT, TOBIAS HUEMPFNER, LENNART VORBRINK, BERND SCHRÖTER, ROMAN FORKER, and TORSTEN FRITZ — Institute of Solid State Physics, Friedrich Schiller University Jena, Helmholtzweg 5, 07743 Jena, Germany

Research on superconductivity in doped polycyclic aromatic hydrocarbons has attracted strong interest in the last few years. Among the investigated molecules potassium-doped 1,2;8,9-dibenzopentacene (DBPen, C₃₀H₁₈) was reported to exhibit one of the highest critical temperatures (33 K) [1]. Nevertheless, there are only few studies regarding its electronic properties. We deposited thin films of DBPen on Ag(111) in the range up to a few monolayers and investigated their behavior after several annealing procedures. Thickness dependent measurements with ultraviolet and x-ray photoelectron spectroscopy (UPS, XPS) were combined with low-energy electron diffraction (LEED) to elucidate the relationship between structural and electronic properties. We observed molecular signatures in the UP spectra which have their origin in different electronic structures of the molecules. These are analyzed under consideration of the LEED patterns that show one rather stable highly ordered phase. The influence of the molecule-substrate interaction on the results will also be discussed.

O 5.10 Mon 12:45 WIL A317

Work function tuning by electron irradiation of aromatic self-assembled monolayers — •ERIC SAUTER¹, CAN YILDIRIM¹, ANDREAS TERFORT², and MICHAEL ZHARNIKOV¹ — ¹Applied Physical Chemistry, Heidelberg University, 69120 Heidelberg, Germany — ²Institut für Anorganische und Analytische Chemie, Universität Frankfurt, Max-von-Laue-Straße 7, 60438 Frankfurt, Germany

Self-assembled monolayers are frequently used to manipulate injection barriers in organic electronics by introduction of a specific dipole moment at the interfaces between the electrodes and adjacent organic layers. This is usually achieved by the selection of a proper dipolar terminal tail group comprising the SAM-ambient interface, which was recently complemented by embedding such a group into the molecular backbone. Here we demonstrate that the work function of SAMs can also be adjusted by electron irradiation in a quite broad range and in controlled fashion, as far as these films contain pyridine or pyrimidine group. This effect is demonstrated by the example of several representative aromatic SAMs with either embedded pyrimidine group or terminal pyridine group. The observed behavior is presumably related to specific chemical transformations involving the nitrogen atom in these moieties. The SAMs with the embedded pyrimidine group are then especially attractive since this moiety is decoupled from the SAM-ambient interface. The effect is especially pronounced as far as it is monitored in situ but is partly quenched upon exposure of the irradiated films to ambient which is attributed to the enhanced reactivity of these films to airborne molecules, above all water.