

O 44: Metal substrates: Adsorption of organic / bio molecules VI

Time: Thursday 10:30–13:00

Location: SCH A118

O 44.1 Thu 10:30 SCH A118

Self-Assembly Induced Chirality in CoTPP on Cu(110) — ●ABEL ROBIN, PHILIP DONOVAN, RASMITA RAVAL, MATTHEW STEPHEN DYER, and MATS PERSSON — University of Liverpool, Liverpool, U.K.

We describe the adsorption of Co(II) tetraphenylporphyrin (CoTPP) on Cu(110) using a combination of STM and periodic DFT. Porphyrins' electronic, magnetic and catalytic properties make them an attractive target for introducing organised functionality at surfaces.

We show that CoTPP forms highly ordered 2D arrays on Cu(110). Importantly, the self-assembled structures exhibit chirality on both organisational and molecular levels, creating equal and opposite mirror domains. The expression of chirality in adsorbed porphyrin systems has only been observed rarely. Here we delineate important factors driving chiral expression in a per se non-chiral system.

DFT shows a strong energetic preference for molecules adsorbing in bridge sites, accompanied by a significant charge exchange between the macrocycle and the substrate. Optimised intermolecular and molecule-substrate interactions rotate and tilt the phenyls, endowing the porphyrins with a propeller-like, thus chiral, conformation. These propeller-like molecules assemble along two non-symmetry directions, leading to large chiral domains mirrored across the main copper axes.

For the predominant structure we distinguish two sets of diametrically opposite phenyls possessing distinct interactions with the substrate. Because of this anisotropy, assembly along one chiral direction is less flexible than along the other. Our DFT calculated images correspond well with the STM images for this structure.

O 44.2 Thu 10:45 SCH A118

SPA-LEED study on metal-free phthalocyanine sub-monolayers on Ag(111) — ●PATRICK BAYERSDORFER¹, INGO KRÖGER¹, FRIEDRICH REINERT^{1,2}, and CHRISTIAN KUMPF^{1,3} — ¹Universität Würzburg, Experimentelle Physik II, D-97074 Würzburg — ²FZ Karlsruhe, Gemeinschaftslabor für Nanoanalytik, D-76021 Karlsruhe — ³FZ Jülich GmbH, IBN-3, D-52425 Jülich

The geometrical alignment of organic molecules in the first adlayer on a surface strongly influences interface properties like surface dipoles or charge transfer, but it also plays an important role for the growth of further molecular layers. Phthalocyanines (Pcs) deposited on a silver surface play a prominent role in this context since they exhibit an unusual adsorption behaviour. We use high-resolution low energy electron diffraction (SPA-LEED) in order to investigate geometrical aspects of metal-free Pc (H2Pc) sub-monolayers on Ag(111). At room temperature (RT) and up to a coverage of 0.75 ML no long range ordered structures occur. The molecules arrange themselves randomly on the surface and maximize the distance to their neighbours. Between 0.75 ML and 0.91 ML a commensurate superstructure is formed followed by a series of continuously changing point-on-line structures above 0.91 ML. The latter superstructures were already observed for metal Pcs in our group (CuPc, SnPc, TiOPc, see contributions of I. Kröger, M. Häming and M. Kochler). They proof the existence of a dominant intermolecular repulsion between the molecules on Ag(111). However, in contrast to the metal Pcs, H2Pc exhibits a commensurate structure also at RT which indicates a reduced intermolecular repulsion.

O 44.3 Thu 11:00 SCH A118

Determining the diffusion coefficients of large organic molecules on a metal surface from tunneling current fluctuations — ●JULIAN IKONOMOV, CHRISTOPH H. SCHMITZ, and MORITZ SOKOLOWSKI — Institut für Physikalische und Theoretische Chemie, Universität Bonn, Wegelerstr. 12, 53115 Bonn, Deutschland

The diffusion of organic molecules on surfaces has so far been mostly investigated by molecule tracking using the video STM technique [1]. This method requires small molecule coverages and small diffusion coefficients. Here we present a new technique suitable for higher temperatures and arbitrarily coverages based on the temporal increase in the tunneling current that occurs when a molecule diffuses under the STM tip. For our measurements, we have chosen the model system perylene-3,4,9,10-tetracarboxylic acid dianhydride (PTCDA) on Ag(100). The PTCDA molecules form highly ordered two-dimensional islands surrounded by gas-like phase [2]. In order to determine the diffusion coefficients, we used a continuum model to describe the diffusion of

the molecules under the tip. Due to the finite size of the molecule it is even possible to obtain the spatial anisotropy of the diffusion coefficient. From the density of the peaks in the current-time spectra, one may in addition quantitatively estimate the tip-molecule interaction and the mean local coverage.

Funded by the DFG through SFB 624.

[1] M. Schunack et al., *Phys. Rev. Lett.*, **88** (2002) 156102.

[2] J. Ikonov et al., *Surf. Sci.*, **602** (2008) 2061.

O 44.4 Thu 11:15 SCH A118

Nature of Free-Electron-Like States in PTCDA molecules Adsorbed on an Ag(111) Surface — ●MATS PERSSON and MATTHEW DYER — Surface Science Research Centre, University of Liverpool, L69 3BX Liverpool, UK

Advances in molecular assembly experiments on metal surfaces and potential applications arising from them call for a better understanding of the electronic structure at the interface of metals and organic systems. There is a high interest in delocalized electronic states, because of their potential use in molecular and opto-electronics applications. Recently, unoccupied, free-electron-like states arising in mono layers of 3,4,9,10-perylene-tetracarboxylic acid dianhydride (PTCDA) molecules adsorbed on an Ag(111) surface at energies close to the Fermi energy have been observed by scanning tunneling and photoemission spectroscopies [1,2]. So as to reveal the nature of these delocalized states we have carried out a density functional study of the electronic structure and local density of states of these systems. We show that the observed free-electron state originates from a Shockley surface state (SS) at the zone centre of the bare surface. The SS is shifted up by the interaction with the organic overlayer. [1] R. Temirov *et al.*, *Nature* **444**, 350 (2006). [2] C. H. Schwalb *et al.*, *Phys. Rev. Lett.* **101**, 146801 (2008).

O 44.5 Thu 11:30 SCH A118

PTCDA chemisorbed on Ag(110): Dispersion interactions and charge equilibration — ●REINHARD SCHOLZ¹ and AFSHIN ABBASI² — ¹Walter Schottky Institut, TU München, Germany — ²Institut für Physik, TU Chemnitz, Germany

The chemisorption of PTCDA on Ag(110) is analysed with 2nd order Møller-Plesset perturbation theory (MP2), accounting therefore for the main part of the dispersion interactions at an *ab initio* level. Irrespective of the size of the rigid silver cluster used as a substrate model, the optimized geometry consists of a nearly flat perylene core, surrounded by carboxylic oxygens closer to the substrate, but with anhydride atoms at a larger height. The charge equilibration between adsorbate and substrate involves charge injection from the oxygen atoms into the substrate, and back transfer of two electrons into the former LUMO of the free molecule. Surprisingly, the resulting negative charge of the adsorbate has a very small contribution in the core region where the main part of the LUMO is localized, but instead accumulates on the end groups. It can be shown in detail that a rehybridization of molecular σ and π states results in a decoupling of several π states on the oxygen atoms from the aromatic core, as opposed to the free molecule, where the π states delocalize over the entire molecule. These decoupled π states on the end groups are forming the binding Ag-O orbitals injecting electronic charge from the molecule into the substrate. Compared to the dominating mechanisms discussed above, the hybridization between orbitals in the core region and the underlying substrate plays only a minor role for the charge balance.

O 44.6 Thu 11:45 SCH A118

Interface states investigated by PES, IPES and 2PPE: the example of PTCDA/Ag — ●ACHIM SCHÖLL¹, STEFAN KRAUSE¹, SÖNKE SACHS¹, JOHANNES ZIROFF¹, CHRISTIAN SCHWALB², MANUEL MARKS², ULRICH HÖFER², EBERHARD UMBACH³, and FRIEDRICH REINERT¹ — ¹Uni Würzburg, Experimentelle Physik II, D-97074 Würzburg — ²Philipps-Uni Marburg, Physik und Materialwissenschaften, D-35032 Marburg — ³FZ Karlsruhe, D-76021 Karlsruhe

We have studied the occupied and unoccupied states at the PTCDA/Ag interface, enabling us to draw a comprehensive picture of the interfacial electronic structure [1]. The strong, unambiguously covalent, interaction leads to hybrid orbitals (interface states), involving at least LUMO, HOMO, and HOMO-1, and Ag 5s- and 4d-states.

The LUMO is pulled below E_F resulting in a new occupied state. High-resolution photoemission (PES) data reveal that on Ag(111) this state is partially filled leading to a "metallic" phase. Inverse PES (IPES) and two-photon photoemission (2PPE) reveal a new unoccupied state 0.6 eV above E_F , which disperses with an effective mass of 0.39 m_e at the Γ -point. The short lifetime (54 fs) indicates a large penetration into the metal. This state is interpreted as predominantly due to an adsorption induced upshift of the Ag(111) Shockley state[2].

These interface states are expected to have notable influence on the charge carrier injection properties at an interface, particularly if their wave function penetrates the metal as well as the molecular layer.

[1] Y. Zou et al., Surf. Science, 2006. 600(6)1240.

[2] C.H. Schwalb et al., Phys. Rev. Lett., 2008. 101(14).

O 44.7 Thu 12:00 SCH A118

PTCDA induced faceting of a vicinal Ag(111) surface: an in-situ LEEM study — ●THOMAS SCHMIDT¹, FLORIAN POLLINGER², HELDER MARCHETTO¹, STEFAN SCHMITT², FLORIAN C. MAIER², ALESSANDRO SALA¹, FRIEDRICH T. REINERT², EBERHARD UMBACH^{2,3}, and HAJO FREUND¹ — ¹Fritz-Haber-Institut, Abt. CP, 14195 Berlin — ²Universität Würzburg, EP II, 97074 Würzburg — ³Forschungszentrum Karlsruhe, 76021 Karlsruhe

Adsorption of organic molecules on vicinal metal surfaces is known to promote faceting and self-organized ordering on mesoscopic scales[1]. In the temperature range between 400 K and 620 K the adsorption of PTCDA on a Ag(10 8 7) surface has been studied in-situ and in real-time by LEEM (low energy electron microscopy) and LEED, using the SMART microscope[2]. The deposition of one organic layer leads to grating-like structures. The direct observation reveals a two-step process: first, facets with an angle of ca. 25° inclination are formed with (111) orientated areas in between, whereas only the facets are covered by PTCDA. In a second step the bare (111) areas are covered by PTCDA, forming a complete monolayer. The temperature dependence of the structure sizes and the influence of inhomogeneity in the initial substrate step density are discussed.

[1] S. Schmitt, Dissertation Würzburg, 2007.

[2] R. Fink et al. J. Electr. Spectrosc. Rel. Phen. 84 (1997) 231-250.

O 44.8 Thu 12:15 SCH A118

Current-induced switching of PTCDA on Ag(111) — ●OLGA NEUCHEVA, CHRISTIAN WEISS, RUSLAN TEMIROV, and FRANK STEFAN TAUTZ — Institut für Bio- und Nanosysteme (IBN-3) and JARA-Fundamental of Future Information Technology, Forschungszentrum Jülich, 52425 Jülich, Germany

A low temperature scanning tunneling microscope (LT-STM) has been used to investigate electron transport through a single PTCDA molecule on Ag(111). Under certain conditions, one of the carboxylic oxygen atoms of the PTCDA molecule establishes a chemical bond with the STM tip, forming a covalently bound single molecular junction [1]. In this contribution, we investigate the process of contact formation as a function of parameters such as distance, bias voltage and electrical current through the molecular junction. In a narrow distance and voltage interval, bistable switching of the oxygen atom between a high- and low-conductance state is observed. The implications of this observation are discussed. [1] Temirov R., Lassise A.,

Anders F.B., et al., Nanotechnology 19 (2008) 065401

O 44.9 Thu 12:30 SCH A118

Influence of dispersion interactions on the adsorption geometry of NTCDA on a (110)-oriented silver substrate — ●AFSHIN ABBASI¹, MICHAEL SCHREIBER¹, and REINHARD SCHOLZ² — ¹Institut für Physik, Technische Universität Chemnitz, D-09107 Chemnitz, Germany — ²Walter Schottky Institut, Technische Universität München, Am Coulombwall 3, D-85748 Garching, Germany

We investigate the adsorption of NTCDA on Ag(110) with second-order Møller-Plesset perturbation theory (MP2) and density functional theory (DFT), using rigid metal clusters of different size as a model for the substrate. In each method, the adsorption geometry depends only weakly on the size of the metal cluster, but both microscopic approaches differ significantly: MP2 gives a nearly flat adsorbate, whereas the lack of dispersion interaction in DFT results in a strongly bended geometry, placing the aromatic core at a much larger distance from the topmost substrate layer with respect to the oxygen groups. Irrespective of the microscopic approach, the carboxylic oxygens interact more strongly with the substrate than the anhydride oxygens, placing them about 0.2 Å closer to the topmost silver layer. On the largest substrate cluster containing 34 silver atoms in three consecutive crystal planes, MP2 places the carbon atoms at an average height of 2.57 Å above the topmost silver layer, about 0.3 Å closer than in the strongly bended geometry geometry obtained with DFT. From these findings, we conclude that the chemisorption geometry of NTCDA on Ag(110) cannot be quantified without the dispersion interactions included at the MP2 level.

O 44.10 Thu 12:45 SCH A118

"Soft" metallic contact to isolated C₆₀ molecules — ●HENDRIK GLOWATZKI¹, BENJAMIN BRÖKER¹, RALF-PETER BLUM¹, OLIVER T. HOFMANN², ANTJE VOLMER³, RALPH RIEGER⁴, KLAUS MÜLLEN⁴, EGBERT ZOJER², JÜRGEN P. RABE¹, and NORBERT KOCH¹ — ¹Humboldt-Universität zu Berlin, Institut für Physik, Berlin, Germany — ²Technische Universität Graz, Institut für Festkörperphysik, Graz, Austria — ³BESSY, Berlin, Germany — ⁴MPI for Polymer Research, Mainz, Germany

We investigated the electronic as well as the structural properties of Hexaazatriphenylene-hexanitrile (HATCN) and C₆₀ on Ag(111) by using ultraviolet photoelectron spectroscopy (UPS) and scanning tunneling microscopy (STM) accordingly. HATCN was used as buffer layer to decouple the test-molecule C₆₀ from the metal substrate. Photoemission revealed metallic behavior of HATCN on Ag(111) which calculations confirmed to be due to partial filling the LUMO of chemisorbed HATCN. From STM a regular honeycomb-structure was found. Using C₆₀ as test-molecule on top of this layer the holes within the honeycombs were acting as adsorption centers leading to laterally spacing between C₆₀ molecules as observed by STM. At the same time UPS revealed virtually bulk like electronic properties of C₆₀ on metallic HATCN/Ag(111) which is in strong contrast to the bare C₆₀-Ag(111) interface being significantly altered by charge transfer. This opens up new possibilities in probing the undisturbed properties of individual molecules on metal substrates. This work is financially supported by European Community project "IControl" (EC-STREP-033197).