

O 56: Metal substrates: Adsorption of organic / bio molecules III

Time: Wednesday 16:45–19:15

Location: A 053

O 56.1 Wed 16:45 A 053

Ruthenium dyes on Au(111) and Ag(111) investigated by scanning tunneling microscopy — ●NADINE HAUPTMANN¹, CHRISTIAN HAMANN¹, FELIX KÖHLER², RAINER HERGES², HAO TANG³, and RICHARD BERNDT¹ — ¹Institut für Experimentelle und Angewandte Physik, Christian-Albrechts-Universität zu Kiel, 24098 Kiel, Germany — ²Otto-Diels-Institut für Organische Chemie, Christian-Albrechts-Universität zu Kiel, 24098 Kiel, Germany — ³CEMES/CNRS, 31055 Toulouse Cedex, France

Ruthenium dyes are promising candidates for sensitizers in dye-sensitized solar cells. We used electrospray ionization to deposit the dyes on Ag(111) and Au(111) surfaces in ultra high vacuum. The structure of the adsorbed molecules was analyzed with low-temperature scanning tunneling microscopy. In addition, scanning tunneling spectroscopy was used to investigate the electronic properties of the ruthenium dyes revealing sharp features in the differential conductance in addition to the HOMO-LUMO gap. Financial support by the Deutsche Forschungsgemeinschaft via the SFB 677 is acknowledged.

O 56.2 Wed 17:00 A 053

Organometallic opto-electronically active magnetic molecules on metallic surfaces — ●CORMAC TOHER, JÖRG MEYER, ANJA NICKEL, ROBIN OHMANN, FRANCESCA MORESCO, and GIANAURELIO CUNIBERTI — Institute for Materials Science and Max Bergmann Center of Biomaterials, TU Dresden, 01062 Dresden, Germany.

Opto-electronically active organic molecules offer several advantages over traditional solid-state semiconductor materials in the fabrication of solar cells, including their low-cost, low weight, and flexibility. Here, we present the results of combined STM and DFT investigations of organometallic optoelectronically active magnetic molecules which are based on aza-BODIPY derivatives. Aza-BODIPY molecules have a tunable infra-red absorption and function as electron donors in organic solar cells [1, 2]. By switching between different central metal atoms such as Co or Zn, both magnetic and non-magnetic examples of this molecule can be synthesized. STS conductance measurements on the magnetic molecules suggest evidence of changes in their spin configuration when an electric field is applied. DFT calculations indicate that this may be due to the electrostatic spin-crossover effect [3].

[1]J. Meyer et. al, Phys. Chem. Chem. Phys. 13, 14421 (2011).

[2]R.Gresser et. al., Chem.-Eur. J. 17, 2939 (2011).

[3]N. Baadji et. al., Nature Materials 8, 813 (2009).

O 56.3 Wed 17:15 A 053

Cysteine on Ag(111) – Chiral self-assembly and temperature-dependant phase-transitions — ●SYBILLE FISCHER¹, ANTHOULA C. PAPAGEORGIOU¹, MATTHIAS MARSCHALL¹, JOACHIM REICHERT¹, KATHARINA DILLER¹, FLORIAN KLAPPENBERGER¹, FRANCESCO ALLEGRETTI¹, ALEXEI NEFEDOV², CHRISTOF WÖLL², and JOHANNES V. BARTH¹ — ¹Physik Department E20, Technische Universität München, 85748 Garching, Germany — ²Institut für Funktionelle Grenzflächen, Karlsruher Institut für Technologie, Hermann-von-Helmholtz-Platz, 76344 Eggenstein-Leopoldshafen, Germany

Understanding the interactions between the chiral amino acid cysteine and metal surfaces is an important step towards creating tailored bio-functionalized surfaces using the molecule's chemical functionalities and medical properties. L-cysteine is involved in the pathogenetic mechanism of HIV [1] as well as in metal interaction centers of many proteins [2]. Being the only proteinogenic amino acid containing a thiol group, cysteine is also used to anchor longer peptides on metal surfaces.

Here a combined STM and XPS study on cysteine is presented. STM measurements at room temperature were carried out on both enantiopure cysteine compounds showing distinctive self-assembly patterns. A phase transformation was discovered after annealing to 400 K. XPS was employed to elucidate the driving force of this transformation. A strong chemical shift of the nitrogen 1s core level revealed a concomitant change of the molecule from a zwitterionic to an anionic state.

[1] Eck, H.-P. et al, *Biol. Chem. Hoppe-Seyler* **1989**, 370, 101–108[2] Barnham, K.J. et al, *Nat. Rev. Drug Discovery* **2004**, 3, 205–214

O 56.4 Wed 17:30 A 053

Orientation-dependent electronic structure of a molecule investigated by STM and DFT with dispersion corrections — ●MAYA LUKAS¹, KARIN FINK¹, KERRIN DÖSSEL¹, ALEXANDRINA STUPARU¹, CHRISTOPHE STROH¹, OLAF FUHR¹, MARCEL MAYOR^{1,2}, and HILBERT VON LÖHNESEN^{1,3} — ¹Karlsruher Institut für Technologie (KIT), Institut für Nanotechnologie, D-76021 Karlsruhe — ²Universität Basel, Department of Chemistry, CH-4056 Basel — ³Karlsruher Institut für Technologie (KIT), Physikalisches Institut und Institut für Festkörperphysik, D-76021 Karlsruhe

In recent years it has become obvious that the exact orientation and bond of a molecular wire to its connecting electrodes has a crucial influence on the molecular conductance. Determining the exact bond configuration as well as the electronic properties within the same experiment is hardly ever achieved, if possible at all.

We investigated a molecule which consists of several identical molecular wires connected in a rigid conformation. Due to the form of the molecule, some of the wires protrude freely from the surface, while others are attached to it. The influence of the coupling to the surface electrode on the position and electronic properties of the molecule is investigated by scanning tunneling microscopy and density functional theory with dispersion corrections. Within the same molecular conformation, chemically identical parts of the molecule with different orientations towards the surface show strong variations of the electronic structure in the experiment as well as in the calculations.

O 56.5 Wed 17:45 A 053

Perylene derivative on Au(111): Influence of a large built-in dipole on molecular assembly and work function — ●JENS NIEDERHAUSEN¹, HEITH KERSELL², HENRIKE WONNEBERGER³, SAW-WAI HLA², JÜRGEN P. RABE¹, KLAUS MÜLLEN³, and NORBERT KOCH¹ — ¹Humboldt-Universität, Institut für Physik, Berlin, Germany — ²Ohio University, Physics & Astronomy Department, Athens, USA — ³Max Planck Institut für Polymerforschung, Mainz, Germany

The anhydride- and diphenylamine-functionalized perylene derivative 9-(bis-p-tert-octylphenyl)-amino-peryene-3, 4-dicarboxy anhydride (ID28) is expected to exhibit a dipole moment as large as 12.2 Debye [1]. When evaporated on Au(111) in ultrahigh vacuum, ID28 molecules adopt a flat-lying conformation in the monolayer regime, as evident by room temperature scanning tunneling microscopy. We analyze the observed packing structures by involving molecule-substrate and molecule-molecule interactions, and the influence of the molecular dipole moment.

The macroscopic surface-normal electrostatic effect of the molecular dipole moment is investigated by ultraviolet photoelectron spectroscopy. The dipole of a monolayer of ID28 molecules shows no significant contribution to the sample work function. However, when going from monolayer to multilayer coverage we find a continuous work function decrease of up to about 1 eV. This is attributed to a preferred orientation of the molecules in multilayers, resulting in a macroscopic dipole pointing away from the sample surface.

[1] T. Edvinsson et al., *J. Phys. Chem. C Letters* 2007, 111, 15137

O 56.6 Wed 18:00 A 053

Charge state of a donor-acceptor complex on the surface of a metal — ●ISABEL FERNANDEZ-TORRENTE, TOBIAS R. UMBACH, ADRIAN OLIVERA, JOSE IGNACIO PASCUAL, and KATHARINA J. FRANKE — Institut für Experimentalphysik, Freie Universität Berlin, Berlin, Germany

The charge state of a molecule has a strong impact on its reactivity and transport properties. We investigate by means of scanning tunneling microscopy (STM) and spectroscopy (STS) the electronic properties of the electron-acceptor 2,3,5,6-Tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4TCNQ) adsorbed on Au(111), and its mixture with the electron-donor tetrathiafulvalene (TTF). Highly ordered pure F4TCNQ islands leave the underlying herringbone reconstruction unaffected. The charge state of the molecule depends strongly on the adsorption site: only the molecules located on the hcp regions are single charged, as demonstrated by the presence of a Kondo resonance in STS experiments. Combined deposition of TTF and F4TCNQ results in the formation of two mixed, ordered phases with 1:1 and 5(F4TCNQ):4(TTF) stoichiometries that destroy the reconstruction of the surface. The F4TCNQ within each unit cell

are not homogeneously coupled to the surface due to the lateral interaction with TTF and, consequently, they exhibit different charge states. Furthermore, STS displays extremely sharp features on the F4TCNQ molecules of this mixed phases that are associated to charging/discharging events in a double barrier tunnelling junction mediated by the electric field of the STM tip.

O 56.7 Wed 18:15 A 053

Site-specific adsorption and reversible switching of C60 on porphyrin double-decker complexes — ●SARANYAN VIJAYARAGHAVAN, DAVID ÉCIIJA, SUSHOBHAN JOSHI, WILLI AUWÄRTER, and JOHANNES V. BARTH — Physik Department E20, Technische Universität München, D-85748 Garching, Germany

Organic solar cells based on donor-acceptor architectures are the next paradigm in photovoltaics taking into account that they are flexible, easier to process than the inorganic counterparts and environmental friendly. Accordingly, a fundamental understanding of molecular donor-acceptor systems is of immense interest for related applications. Here, we report a scanning tunneling microscopy (STM) and spectroscopy (STS) study characterizing C60 molecules on CeTPP2 arrays on a Ag(111) substrate. At low coverage and temperature, the C60s adsorb on the center of the top porphyrin of the CeTPP2, thus forming non-covalent porphyrin-C60 dyads. The STS measurements indicate a weak coupling of the C60 to the Ag substrate, as evidenced by a large HOMO-LUMO gap and a negative differential resistance regime. High-resolution images resolve three distinct orientations of the C60 on CeTPP2. By applying a current pulse with the STM tip, it is possible to switch individual C60s between these three configurations without changing the lateral registry. A plot of tunneling current vs. time reveals three levels of conductance. Each level corresponds to one of the distinct C60 orientations and thus represents a specific intra-dyad coupling

O 56.8 Wed 18:30 A 053

Tuning the electronic and magnetic properties of adsorbed Co porphyrin molecules by NO as an axial ligand — ●CHRISTIAN FELIX HERMANN, MATTHIAS BERNIEN, ALEX KRÜGER, JORGE MIGUEL, and WOLFGANG KUCH — Freie Universität Berlin, Arnimallee 14, 14195 Berlin, Germany

Metalloporphyrin molecules consist of a metal ion, surrounded by a planar porphyrin ligand and two axial coordination sites, which can be occupied by additional ligands like small molecules or a metal surface. This allows to tune the electronic and magnetic properties of the ion.

Here, we report on X-ray absorption spectroscopy (XAS) measurements of submonolayers of Co octaethylporphyrin (CoOEP) molecules and NO-CoOEP nitrosyl complexes on bare and oxygen-covered Ni films grown on Cu(100). Angle-dependent N K edge XAS measurements reveal a quasi-flat adsorption of CoOEP on both substrates.

By means of Co $L_{3,2}$ X-ray magnetic circular dichroism (XMCD) spectra we demonstrate, how the ferromagnetic substrate, as an additional ligand to the CoOEP molecules, induces a magnetic ordering on the spins of the Co ions, which are on both substrates parallel aligned to the Ni magnetization. The adsorption and thermal desorption of NO, as second axial ligand to CoOEP enables the reversible switching

of the electronic properties of the Co ions on the oxygen-covered Ni films. On both substrates, angle-dependent Co $L_{2,3}$ XAS measurements reveal different oxidation states of the Co ions of CoOEP and NO-CoOEP.

This work is supported by the DFG (Sfb 658).

O 56.9 Wed 18:45 A 053

Free-base porphine on Ag(111): Repulsive interaction and substrate mediated phase transitions. — ●FELIX BISCHOFF, WILLI AUWÄRTER, DAVID ÉCIIJA, SARANYAN VIJAYARAGHAVAN, SUSHOBHAN JOSHI, KNUD SEUFERT, and JOHANNES V. BARTH — Physik Department, E20, TU München, Germany

Motivated by nature, porphyrins have been established as useful building blocks in functional nano-architectures. A key issue is the tailoring of porphyrin building blocks with desired properties, yet a detailed understanding of the influences of different constituents, such as meso-substituents and central metal ions, is still lacking. To advance the control of surface-confined porphyrins, we studied the simplest molecule - the porphine - that is the basic macrocyclic body of all porphyrins. We present systematic low-temperature STM experiments of free-base porphines (2H-P) on Ag(111). At low coverages, porphines exhibit a disordered phase, indicating repulsive electrostatic interactions that could arise from charge-transfer bonds with the metal substrate. The molecules are selectively chemisorbed at specific adsorption sites. This also causes substrate-mediated phase transitions with increasing coverage from a disordered lattice gas, to a liquid-like phase, to a regular solid and finally to a glassy layer that shows an average positional, but no orientational order.

O 56.10 Wed 19:00 A 053

2D glassy crystals from flexible molecular modules — ●DAVID ECIIJA¹, SARANYAN VIJAYARAGHAVAN¹, WILLI AUWÄRTER¹, SUSHOBHAN JOSHI¹, KNUD SEUFERT¹, CLAUDIA AURISICCHIO², DAVIDE BONIFAZI², and JOHANNES V. BARTH¹ — ¹Physik Department E20, Technische Universität München, D-85748 Garching, Germany — ²University of Namur, Department of Chemistry, B-5000 Namur, Belgium

Molecular glassy crystals are materials where the constituents are positioned in registry with a periodic crystalline lattice, but the molecular units are disordered regarding their orientational degrees of freedom. Here, to our knowledge, we present for the first time a two-dimensional (2D) analogue of the three-dimensional glassy crystal state of matter, i.e. a 2D glassy crystal. In particular, the deposition of a flexible molecular module on Cu(111) gives rise to distinct phases whose characteristics have been examined in real space by scanning tunneling microscopy: a hitherto unrecognized 2D conformational glassy crystal and a 2D orientational glassy crystal, respectively. Herein, the 2D conformational glassy crystalline phase constitutes a novel organization of matter, which combines local conformational disorder and translational symmetry. Both phases are porous and exhibit an arrangement of nanopores that are stabilized by the simultaneous presence of pyridyl-Cu-pyridyl links and C-H^{***}N interactions. In the 2D conformational glassy crystal the framework displayed unprecedented flexibility as probed by the STM tip that modifies the pore shape, a prerequisite for adaptive behavior in host-guest processes.