

O 27: Organic/bio Molecules on Metal Surfaces III

Time: Tuesday 10:30–13:15

Location: TRE Phy

O 27.1 Tue 10:30 TRE Phy

Kondo effect in PTCDA/Au(111) induced by doping with single gold atoms — ●TANER ESAT¹, CHRISTIAN WAGNER¹, RUSLAN TEMIROV¹, STEFAN TAUTZ¹, THORSTEN DEILMANN², PETER KRÜGER², and MICHAEL ROHLFING² — ¹Peter Grünberg Institute (PGI-3), Forschungszentrum Jülich, Germany — ²Institut für Festkörpertheorie, Universität Münster, D-48149 Münster, Germany

Interest in molecular magnets has been growing rapidly for the last few years. Understanding and gaining control over their properties might open a route to nanospintronics and quantum computing. One of the interesting possibilities to tune the magnetic properties of molecules is by controlled charge transfer from other molecules [1] or metal surfaces [2]. In this work we show another approach by doping non-magnetic molecules physisorbed on metal surfaces with single metal atoms.

By means of LT-STM and STS we have investigated the adsorption of single Au adatoms on a PTCDA monolayer adsorbed on a Au(111) surface.

We find two different types of Au adatoms on PTCDA which differ in their STS spectra and apparent size in the STM images. Both types show a pronounced peak in dI/dV conductance at zero bias. Temperature dependent measurements of FWHM and height of the zero-bias conductance peak confirm that the peak originates from the Kondo effect with a corresponding Kondo temperature of 37.5 ± 6.5 K.

[1] I. Fernández-Torrente et al., Phys. Rev. Lett. 108, 036801 (2012)

[2] R. Temirov et al., Nanotechnology 19 (6), 065401 (2008)

O 27.2 Tue 10:45 TRE Phy

A single Au adatom on PTCDA: Au(111) – results from ab-initio calculations — ●THORSTEN DEILMANN¹, PETER KRÜGER¹, MICHAEL ROHLFING¹, TANER ESAT², CHRISTIAN WAGNER², RUSLAN TEMIROV², and STEFAN TAUTZ² — ¹Institut für Festkörpertheorie, Universität Münster, D-48149 Münster, Germany — ²Peter Grünberg Institute (PGI-3), Forschungszentrum Jülich, Germany

The electronic properties of organic adsorbates on a noble-metal surface depend on structural and environmental details [1].

Here we investigate the influence of an additional Au adatom on a PTCDA monolayer that is adsorbed on a Au(111) surface. Adsorption structures, electronic spectra and scanning tunneling microscopy (STM) images are calculated within density-functional theory.

The weak binding of PTCDA on Au(111) leads to a large bond distance of more than 3 Å between the molecule and the substrate. We investigate different conceivable adsorption sites for the Au adatom above PTCDA. The most favorable adatom position is about 2 Å above the PTCDA molecule. Alternatively, an Au adatom can be located in the region between the molecules. The electronic structure around E_F shows distinct differences for the two adsorption sites. If the adatom is above a PTCDA molecule a dominant maximum above the Au adatom is visible in the calculated STM image.

[1] A. Greuling et al., Physica Status Solidi B 250, 2386 (2013).

O 27.3 Tue 11:00 TRE Phy

Gold-Adatom-Mediated Bonding and Molecular Orbital Redistribution in Metal-Organic Chains — ●ZECHAO YANG¹, MARTINA CORSO^{1,2}, CHRISTIAN LOTZE¹, ELENA MENA-OSTERITZ³, PETER BÄUERLE³, KATHARINA J. FRANKE¹, and JOSE I. PASCUAL^{1,2} — ¹Institut für Experimentalphysik, Freie Universität Berlin, Arnimallee 14, 14195 Berlin, Germany — ²CIC nanoGune, 20018 Donostia-San Sebastián, Spain — ³Institute of Organic Chemistry II and Advanced Materials, University of Ulm, Germany

Dicyanovinyl-quinquephenes (DCV5T-Me2) is a prototype molecule for organic electronics. Here, we investigated the structural and electronic properties of DCV5T-Me2 molecules on Au(111) using low temperature scanning tunneling microscopy and atomic force microscopy. DCV5T-Me2 self-assembles in chains, stabilized by intercalated Au atoms. The spectroscopic fingerprint of the incorporation of Au adatoms is an energetic downshift of the lowest unoccupied molecular orbital of the molecules within the chains with respect to uncoordinated molecules due to metal-ligand hybridization. An asymmetric coordination of the molecule by gold atoms from only one side, leads to an asymmetric orbital shape along the molecule. It is attributed to a redistribution of charge over the molecule as a consequence of a localized coordination bond to the gold atom,

as confirmed by density functional theory calculations. Our study demonstrates that one can manipulate molecular orbital alignments and distribution simultaneously within individual molecules by contacting metal atoms.

O 27.4 Tue 11:15 TRE Phy

Porphyrin metalation providing an example of a redox reaction facilitated by a surface reconstruction — ●JAN NOWAKOWSKI¹, CHRISTIAN WÄCKERLIN¹, JAN GIROVSKY¹, DOROTA SIEWERT¹, THOMAS A. JUNG¹, and NIRMALYA BALLAV² — ¹PSI, Villigen, Switzerland — ²IISER, Pune, India

Recently, significant attention has been drawn to on-surface reactions [1], including on-surface redox chemistry [2], of which the metalation of free-base porphyrins is an interesting example [3, 4]. The on-surface metalation can be realized in three ways: (i) by picking up free heteroatoms from a surface [5]; (ii) by depositing metal atoms on top of molecules predeposited on an inert substrate (e.g. Au or Ag); or (iii) self-metalation, i.e. by coordination with atoms of a crystalline substrate. The temperature of on-surface metalation depends on the method chosen and on the element used [5]. We show [5] that, surprisingly, passivating a Cu(001) surface with an oxygen-surface reconstruction lowers the self-metalation temperature of 5,10,15,20-Tetraphenylporphyrin (2HTPP) from 450 K on native Cu(001) surface to 285 K on the oxygen-reconstructed Cu(001) surface. In the presented study X-Ray Photoelectron Spectroscopy (XPS) and Scanning Tunneling Microscopy (STM) methods have been used.

[1] C. Diaz et al., Science, 2009, 326, 832;

[2] D.-T. Pham et al., New J. Chem., 2006, 30, 1439;

[3] W. Auwärter et al., ChemPhysChem, 2007, 8, 250;

[4] J. M. Gottfried et al., J. Am. Chem. Soc., 2006, 128, 5644;

[5] J. Nowakowski et al., Chem. Commun., 2013, 49, 2347.

O 27.5 Tue 11:30 TRE Phy

NTCDA and CuPc heteroorganic phases on Ag (111) — ●SONJA SCHRÖDER, BENJAMIN STADTMÜLLER, FRANCOIS C. BOCQUET, CAROLINE HENNEKE, CHRISTOPH KLEIMANN, SERGUEI SOUBATCH, FRANK STEFAN TAUTZ, and CHRISTIAN KUMPF — Peter Grünberg Institute (PGI-3), Forschungszentrum Jülich, Germany and Jülich Aachen Research Alliance Fundamentals of Future Information Technology, Jülich, Germany

While in the last decade most studies of organic adsorbates on metal surfaces concentrated on homomolecular systems, recently also heteromolecular thin films moved into the focus of interest. In particular, acceptor-donor systems have considerable potential for future organic devices. Here we report on the heteroorganic system NTCDA and CuPc on Ag(111). In comparison to the system PTCDA+CuPc/Ag(111) investigated earlier [1], the acceptor strength of the charge accepting molecule is weakened by replacing PTCDA by NTCDA. We have investigated the consequences of this manipulation by means of SPA-LEED, NIXSW, UPS and ARPES. As for the PTCDA-CuPc system three mixed structures with different stoichiometric ratios were found: A NTCDA-rich, a *1:1*, and a CuPc-rich phase. In this presentation we concentrate on the lateral and vertical structure formation and show some results from our electron spectroscopic investigations. [1] B. Stadtmüller, D. Lüftner, M. Willenbockel, E.M. Reinisch, T. Sueyoshi, G. Koller, S. Soubatch, M.G. Ramsey, P. Puschnig, F.S. Tautz, C. Kumpf, to be published.

O 27.6 Tue 11:45 TRE Phy

Interaction of a Kondo impurity with its molecular ligand — ●JÖRG MEYER, ANJA NICKEL, ROBIN OHMANN, LOKA MANI, CORMAC TOHER, DMITRY RYNDYK, FRANCESCA MORESCO, and GIANAURELIO CUNIBERTI — Institute for Materials Science and Max Bergmann Center of Biomaterials, Center for Advancing Electronics Dresden, TU Dresden, 01062 Dresden, Germany

We investigated a Co containing organic molecule on different metal surfaces by STM and STS. On Ag(100) the molecule showed a prominent asymmetric peak at the Fermi level. To verify the Kondo nature of this peak, temperature dependent STS was applied and the resulting spectra were fitted with the Fano formula. Afterwards, we measured a grid of spectra with submolecular resolution to determine the shape of the Kondo resonance in different spots of the molecule. Interest-

ingly, the asymmetry/Fano parameter q strongly changed around the molecule in a clearly non-radially symmetric fashion, representing the influence of the molecular ligand on the resonances appearance. This is interpreted as signal transduction of the Kondo resonance via the molecular orbitals. Simulations to support this hypothesis are still ongoing. The strong influence of the local environment is further illustrated by the disappearance of the Kondo resonance on Cu(110). Instead of the asymmetric peak at the Fermi level we found a symmetric peak at -0.2 V. A dI/dV map of these states show the same spatial distribution like the Kondo resonance at the Fermi Level obtained from the speckle measurements.

O 27.7 Tue 12:00 TRE Phy

Structural and optical investigation of ultra-thin layers of potassium doped PTCDA on Ag(111) — ●MARCO GRUENEWALD, CHRISTIAN ZWICK, ROMAN FORKER, and TORSTEN FRITZ — Friedrich-Schiller University Jena, Institute of Solid State Physics, Max-Wien-Platz 1, Jena 07743, Germany

Here we report on the influence of potassium doping on highly-ordered ultra-thin layers of the dye molecule 3,4,9,10-perylene-tetracarboxylic-dianhydride (PTCDA) on Ag(111). The doped thin films have been structurally characterized by LEED and LT-STM as well as optically by in-situ differential reflectance spectroscopy (DRS) [1,2]. We found that potassium doping of submonolayers of PTCDA on Ag(111) induces different highly ordered phases of PTCDA-potassium complexes depending on the doping concentration. Consequently, the electronic and thus optical characteristics of the thin film changes dramatically. For instance, by applying DRS during the film growth and the subsequent doping process we found distinct optical fingerprints which can be partially assigned to anionic features of PTCDA showing different doping stages (as investigated in detail on an inert mica substrate in ref. [3]). Furthermore, structural relaxation of PTCDA-potassium complexes due to annealing will be discussed.

References: [1] R. Forker et al., *Annu. Rep. Prog. Chem., Sect. C: Phys. Chem.*, 2012, 108, 34-68. [2] R. Forker and T. Fritz, *Phys. Chem. Chem. Phys.*, 2009, 11, 2142-2155. [3] T. Dienel et al., *Adv. Mater.*, 2010, 22, 4064-4070.

O 27.8 Tue 12:15 TRE Phy

Temperature-induced Structural and Chemical Changes of Ultrathin Ethylene Carbonate Films on Cu(111) — ●FLORIAN BUCHNER¹, MARAL BOZORGCHENANI^{1,2}, HANIEH FARKHONDEH^{1,2}, BENEDIKT UHL^{1,2}, and R. JÜRGEN BEHM^{1,2} — ¹Helmholtz Institute Ulm (HIU), Ulm, Germany — ²Ulm University, Institute of Surface Chemistry and Catalysis, Ulm, Germany

Ethylene Carbonate (EC) is a key component in Li-ion battery electrolyte. A molecular scale understanding of the solid-electrolyte interphase (SEI) is crucial to improve the Li-ion battery performance. The adsorption and reaction of EC on Cu(111), as a model system, was investigated with scanning tunnelling microscopy (STM) and X-ray photoelectron spectroscopy (XPS) under ultrahigh vacuum (UHV) conditions. Highly ordered 2D EC islands were obtained on Cu(111) at submonolayer and monolayer coverage by STM for adsorption at around 100 K. The adsorption behaviour is discussed in terms of intermolecular interactions and mobility on the surface. The XP C1s and O1s core level spectra prove the adsorption of intact EC molecules. Between 80 K and 420 K, significant structural and chemical changes were detected. Upon heating to room temperature, a highly mobile molecular adlayer is detected by STM. Upon post annealing and cool down to around 100 K a transformation from 2D EC islands into islands with arbitrary shapes is observed. Variable temperature XPS resolves chemical changes of the adlayer upon heating, including desorption of molecular species and decomposition of EC into new surface species.

O 27.9 Tue 12:30 TRE Phy

Resonant tunnelling observed in metal-PTCDA-metal junction — ●MATTHEW GREEN, ALEXANDER GRÖTSCH, RUSLAN TEMIROV, and STEFAN TAUTZ — Peter Grünberg Institut (PGI-3),

Forschungszentrum Jülich, Germany

Understanding of charge transport in single molecule junctions is of fundamental importance, especially for future molecular electronics applications. Single molecules have been shown to conduct electric current, but there is relatively little understanding of the precise charge transport mechanisms responsible for conductance in single molecule junctions. Here we describe a new insight into quantum transport through a single PTCDA molecule suspended between two metal electrodes, namely an atomically clean metal surface and the tip of a combined NC-AFM/STM [1][2]. We are able to probe transport characteristics across a wide range of applied bias voltages. In particular, resonant tunnelling through the lowest unoccupied molecular orbital is observed. Our findings open up the possibility to a more detailed understanding of different charge transport regimes present in single molecule junctions.

[1] N. Fournier et al., *Phys. Rev. B* 84(3) 035435 (2011)

[2] C. Wagner et al., *Phys. Rev. Lett.* 109(7) 076102 (2012)

O 27.10 Tue 12:45 TRE Phy

Stiffness and Electronic Properties of a Single-Molecule Wire — ●CHRISTIAN LOTZE¹, MARTINA CORSO², JINGCHENG LI², GUNNAR SCHULZE¹, THOMAS NIEHAUS³, ALESSANDRO PECCHIA⁴, KATHARINA J. FRANKE¹, and NACHO PASCUAL^{2,5} — ¹Freie Universität Berlin — ²CIC nanoGune, Donostia-San Sebastian, Spain — ³Universität Regensburg — ⁴CNR-ISMN, Rome, Italy — ⁵IKERBASQUE, Bilbao, Spain

Understanding and controlling charge transport properties in single-molecule devices is of great interest, for example to realize future molecular electronic circuits. These properties may change under external stimuli, e.g. light irradiation, electric field or mechanical stress [1]. In our experiments we measure the stiffness and electronic properties of a wire consisting of a single molecule by means of combined Scanning Tunneling and Atomic Force Microscopy (STM/AFM) [2]. With our STM tip we contact a functionalized polyphenyl molecule in one side and lift it up from the surface, while the other side remains attached to the substrate [3]. During lift up we observe characteristic features in the molecule's conductance and find these correlated with plastic changes of the molecular junction. In agreement with DFT simulations we identify the creation of bonds as their origin and can draw a detailed picture of the lifting process of a single-molecule wire. [1] Briechele *et al.*, *Beilstein J. Nanotechnol.* 2012, 3, 798 [2] Giessibl, *Reviews of Modern Physics*, 75, 949 (2003) [3] F. Pump *et al.*, *Appl. Phys. A* 93, 335 (2008)

O 27.11 Tue 13:00 TRE Phy

Force and Conductance in a Single Molecule Junction: SnPc on Ag(111) — ●NUALA M. CAFFREY, CESAR LAZO, PAOLO FERRIANI, and STEFAN HEINZE — Institut für Theoretische Physik und Astrophysik, Christian-Albrecht-Universität zu Kiel, D-24098 Kiel, Germany

Characterisation of the relationship between chemical force and electronic transport in an atomic scale junction is now possible with the combination of scanning tunnelling microscopy (STM) and atomic force microscopy (AFM) (e.g. [1]). Recent work in this area has concentrated mainly on atomic point contacts [2]. In this contribution, we determine, using density functional theory (DFT), the force experienced by an STM tip as it approaches the bistable tin-pthalocyanine (SnPc) molecule adsorbed on a Ag(111) surface. This molecule has been experimentally shown to have one of two possible conformations upon adsorption – either with the central Sn atom pointing away from (SnPc-up) or towards (SnPc-down) the surface [3]. We calculate the electronic transport through both conformations as a function of tip-molecule distance, i.e., in both the tunnelling and contact regime. We calculate the extent of the structural relaxations' contribution to both the force and conductance and furthermore extract the correlation between the two.

[1] Hauptmann et al., *New J Phys.* 14, 073032 (2012)

[2] Ternes et al., *Phys. Rev. Lett.* 106, 016802 (2011)

[3] Wang et al., *J. Am. Chem. Soc.* 131, 3639 (2009)