

O 75: Organic/bio Molecules on Metal Surfaces VI

Time: Thursday 16:00–19:15

Location: H38

O 75.1 Thu 16:00 H38

Bonding and chemical transformations of free-base porphyrin species on Ag(111) — ●ALISSA WIENGARTEN, KNUD SEUFERT, WILLI AUWÄRTER, DAVID ÉCIJA, SUSHOBHAN JOSHI, and JOHANNES V. BARTH — Physik Department E20, Technische Universität München, D-85748 Garching, Germany

Porphyrins play a key role in many biological processes and are promising building blocks for technical applications. Depending on their substitution and the variation of the metal-center incorporated into the macrocycle, the functionality of these molecules can be tuned. A starting point for a systematic investigation of this class of molecules is the fundamental building block for all porphyrin derivatives, the free-base porphine, forming the macrocycle. In this work we study temperature-induced covalent coupling of free-base porphines on the Ag(111) surface via low temperature scanning tunneling microscopy (LT-STM) in ultra high vacuum (UHV). We find that porphines can dehydrogenate and form direct C-C bonds on a hot surface. With increasing sample temperature the number of covalently bound oligomers increases. A further step focuses on the investigation of tetraphenyl-porphyrins on Ag(111), where the molecule shows a so called saddle-shape deformation. Similar to the porphine case annealing induces dehydrogenation reactions resulting in the formation of different porphyrin-derivatives lying flat on the surface.

O 75.2 Thu 16:15 H38

Tuning the Kondo screening of an Fe-Porphyrin molecule by on-surface ligand modification — ●BENJAMIN W. HEINRICH¹, GELAVIZH AHMADI¹, VALENTIN MÜLLER¹, JOSÉ I. PASCUAL^{1,2}, and KATHARINA J. FRANKE¹ — ¹Institut für Experimentalphysik, Freie Universität Berlin, Germany — ²CIC nanoGUNE, 20018 Donostia-San Sebastián, Spain

The structure of the organic ligand in metal-organic complexes governs the adsorption on a metal surface, and thereby, the magnetic interaction between the central ion and the conduction electrons. We use Scanning Tunneling Microscopy and Spectroscopy (STM/STS) at 4.5 K to show how the modification of the ligand structure alters the Kondo screening of an Fe-Porphyrin on Au(111). Annealing Fe(II)-Octaethylporphyrin (FeOEP) on Au(111) to temperatures of about 470 K, we step-wise induce an electrocyclic ring closure of the ethyl groups to finally produce Fe-Tetrabenzoporphyrin (FeTBP). In STS, complex features at low energies around the Fermi level result from Kondo screening of the iron ion's spin. Changes in width and shape show the tuned interaction of the local spin with the conduction electrons depending on the actual chemical structure of the ligand. These results highlight the importance of chemical engineering for controlling the magnetism of single molecules on surfaces.

O 75.3 Thu 16:30 H38

Temperature-Dependent Chemical and Structural Transformations from 2H-Tetraphenylporphyrin to Copper(II)-Tetraphenylporphyrin on Cu(111) — ●STEFANIE DITZE, MICHAEL STARK, JIE XIAO, MICHAEL RÖCKERT, MARTIN DROST, FLORIAN BUCHNER, OLE LYTKEN, HANS-PETER STEINRÜCK, and HUBERTUS MARBACH — Lehrstuhl für Physikalische Chemie II and Interdisciplinary Center for Molecular Materials (ICMM), Universität Erlangen-Nürnberg, Egerlandstr. 3, D-91058 Erlangen

Temperature-driven chemical and structural changes of 2H-Tetraphenylporphyrin (2HTPP) adsorbed on Cu(111) have been investigated by a combination of scanning tunneling microscopy (STM) and X-ray photoemission spectroscopy (XPS) under UHV conditions. The first chemical change is a redox reaction of the porphyrin center with Cu atoms from the substrate, resulting in the formation of Copper(II)-Tetraphenylporphyrin (CuTPP). For a coverage of about 0.17 molecules/nm², this reaction was found to start around 400 K and can easily be monitored by STM, due the very different adsorption behavior of 2HTPP and CuTPP on Cu(111). The energetic parameters of this self-metalation reaction were determined by isothermal STM experiments.[1] Subsequent annealing to 450 and 500 K leads to two intramolecular structural changes, which are attributed to successive dehydrogenation reactions of CuTPP.[2]

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[1] S. Ditze et al. *Angew. Chem. Int. Ed.* 2012, 51, 10898-10901 [2]

Xiao et al. *J. Phys. Chem. C* 2012, 116, 12275-12282

O 75.4 Thu 16:45 H38

Coverage-dependent metalation of tetraphenylporphyrin with Cu(111) — ●MICHAEL RÖCKERT, JIE XIAO, STEFANIE DITZE, MICHAEL STARK, MATHIAS GRABAU, HUBERTUS MARBACH, HANS-PETER STEINRÜCK, and OLE LYTKEN — LS für PC II, Universität Erlangen-Nürnberg, Egerlandstraße 3, D-91058 Erlangen

The coverage-dependent metalation of tetraphenylporphyrin (2HTPP) with Cu atoms from a Cu(111) substrate has been investigated by X-ray photoemission spectroscopy (XPS) and scanning tunneling microscopy (STM) from submonolayer to multilayer coverages. At coverages below 0.17 molecules/nm² the rate of metalation is modest and follows a first order behaviour. However, as the coverage is increased beyond 0.35 molecules/nm² a strong increase in the rate of metalation is observed, and the rate no longer follows a simple first order behaviour. This behaviour is accompanied by the appearance of a checkerboard structure at coverages above 0.35 molecules/nm² as found by STM. Temperature-dependent rates of metalation have been measured for both high (>0.35 molecules/nm²) and low (<0.35 molecules/nm²) coverage, and, based on Arrhenius analyses, prefactors and activation energies for the two reaction channels have been extracted. It was found that the metalation reaction for the high-coverage checkerboard structure had a significantly lower activation energy compared with coverages below 0.17 molecules/nm². The reason for the increased reactivity could be easier access of copper adatoms to the slightly elevated porphyrin molecules in the checkerboard structure.

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O 75.5 Thu 17:00 H38

Ab initio study of CoTPP on coinage metal surfaces — ●TORSTEN HOUWAART and MARIE-LAURE BOCQUET — Laboratoire de Chimie, 46 allée d'Italie, 69364 Lyon cedex 07

Metal-Tetra-Phenyl-Porphyrins (MeTPP) are large π -conjugated molecules which are prevalent in nature. These molecules have applications in many fields of physics and chemistry. We analyze MeTPPs on metallic substrates for its possible application as a gas sensing system or in optoelectronics.

From Scanning-Tunneling-Microscopy experiments it is well known that MeTPPs undergo a deformation on a metallic substrate. We analyze the geometry of the molecule after adsorption as the deformation of porphyrins from a planar shape is believed to have an influence on the reactivity. In this ab-initio study with the density functional code VASP we analyzed the binding site of Cobalt-TPP on Cu(111) with the local density approximation (LDA) and the generalized gradient approximation (GGA) of Perdew, Burke and Ernzerhof (PBE) with and without semi-empirical dispersion (D2) correction by Grimme. From a theoreticians point of view it is important to understand the effect of using different exchange-correlation functionals for the calculation of these systems and the resulting geometries and electronic structure. By looking at changes to the electronic structure of the system the bonding mechanisms on the different binding sites were analyzed.

O 75.6 Thu 17:15 H38

Investigation of the influence of hydrogen bonding on the self-assembled molecular adsorbate structure and manipulation of the electronic structure of tetra(p-hydroxyphenyl)porphyrin — ●LARS SMYKALLA¹, MICHAEL HIETSCHOLD¹, CAROLA MENDE², and HEINRICH LANG² — ¹Chemnitz University of Technology, Institute of Physics, D-09107 Chemnitz, Germany — ²Chemnitz University of Technology, Institute of Chemistry, D-09107 Chemnitz, Germany

Combining scanning tunneling microscopy (STM), scanning tunneling spectroscopy (STS), photoemission spectroscopy (PES) and density functional theory (DFT), we present a thorough study of the adsorption of tetra(p-hydroxyphenyl)porphyrin (H₂THyPP) on crystalline metal substrates. The observed molecular arrangements on Au(111) and the more anisotropic Ag(110) are explained in terms of epitaxy and intermolecular weak hydrogen bonding. Furthermore, the influence of the substrates on the electronic structure of the adsorbed molecules is discussed. The electronic states of the molecule are studied with high spatial resolution using voltage-dependent STM and STS in ultra-high

vacuum, whereby two different kinds of molecular appearances at constant voltage in a monolayer are observed. Further, we are able to switch the molecular contrast of single molecules under the STM tip by voltage pulses. To understand the nature of this change in electronic structure of the molecule we applied density functional theory calculations, which indicate that we find on the surfaces the free-base H₂ThyPP as well as its deprotonated form (without the two hydrogen atoms in the center of the molecule).

O 75.7 Thu 17:30 H38

Assembly, electronic structure and metal-ligand interaction of di-carbonitrile quaterphenyls on an electronically corrugated boron nitride monolayer. — •TOBIAS HOH¹, SUSHOBHAN JOSHI¹, WILLI AUWÄRTER¹, CARLOS-ANDRES PALMA¹, FLORIAN KLAPPENBERGER¹, DAVID ÉCIJA¹, ALISSA WIENGARTEN¹, HERMANN SACHDEV², and JOHANNES V. BARTH¹ — ¹Physik Department, E20, TU München, Germany — ²Max-Planck-Institut für Polymerforschung, Germany

Metal-directed assembly at interfaces is important for the engineering of nanostructures. For molecules on metal surfaces, the presence of substrate electrons can lead to strong perturbations of the electronic structure and unique coordination motifs. Here, we present a low temperature scanning tunneling microscopy (STM) study of di-carbonitrile quaterphenyl molecules on an insulating boron nitride (BN) monolayer grown on Cu(111)[1]. The molecules form a dense packed chevron assembly in contrast to open porous pattern observed on Ag(111)[2]. STM images show a nonplanar conformation corroborated by a molecular dynamics simulation. Tunneling spectroscopy evidences decoupling of the molecules from the metal. Moreover, the inhomogeneous BN template induces a spatial modulation of the energy of unoccupied molecular orbitals. A subsequent deposition of cobalt atoms generates a four-fold coordination motif.

[1] Joshi, S. et al., Nano Lett. 2012, 12, 5821-5828

[2] Schlickum, V. et al., J. AM. CHEM. SOC. 2008, 130, 11778-11782

O 75.8 Thu 17:45 H38

2D lanthanide networks — •JOSE I. URGEL¹, DAVID ÉCIJA¹, ANTHOULA C. PAPAGEORGIOU¹, SARANYAN VIJAYARAGHAVAN¹, SUSHOBHAN JOSHI¹, WILLI AUWÄRTER¹, SVETLANA KLYATSKAYA², MARIO RUBEN², SYBILLE FISCHER¹, JOACHIM REICHERT¹, and JOHANNES V. BARTH¹ — ¹Physik Department E20, Technische Universität München, D-85748 Garching, Germany — ²Karlsruhe Institut für Technologie D-76344 Eggenstein-Leopoldshafen, Germany

Surface-confined metal organic architectures have been recently studied for alkali and transition metals in 2D. However, the field of lanthanide based networks on surfaces remains largely unexplored. Here we present, using scanning tunneling microscopy (STM), a distinct coordination of dicarbonitrile-oligophenyl linkers (p-NC-(Ph)_n-CN-p (n=3,4)) to cerium centers on Ag (111), exhibiting a flexible five-fold nodal motif. By carefully tuning the concentration and the stoichiometric ratio of the rare-earth metal centers and molecular linkers, we realized a 2D hierarchic metal-organic assembly based on dodecameric units. For an increase in the cerium supply, a fully reticulated 2D metal-organic network evolves, whereby linkers are connected on both sides to Ce centers, following a design pattern identified as a molecular Archimedean snub square tessellation of the surface. Our study introduces the first implementation of the f-block elements in 2D metallocsupramolecular assembly.

O 75.9 Thu 18:00 H38

Molecular structure elucidation by atomic force microscopy — •BRUNO SCHULER, LEO GROSS, FABIAN MOHN, and GERHARD MEYER — IBM Research - Zurich, 8803 Rüschlikon, Switzerland

Atomic force microscopy (AFM) offers a completely new and direct approach to investigate the chemical structure of individual molecules [1,2] beside commonly used characterization methods including mass spectrometry, spectroscopic techniques or X-ray crystallography. The capabilities and challenges of AFM-based molecular structure identification were demonstrated on a natural product with previously unknown structure. By combining standard experimental and computational techniques together with AFM the structure was solved and revealed a new structural molecule class [3]. The molecule was studied in UHV at low temperatures on a Cu(111) substrate partially covered with a thin film of NaCl. We used noncontact AFM in the dynamic mode [4] and a qPlus force sensor design [5], where the tip apex was functionalized with a CO molecule [6].

References:

- [1] L. Gross et al., Science 325, 1110 (2009)
- [2] L. Gross et al., Nature Chem. 2, 821 (2010)
- [3] K.O. Hanssen et al., Angew. Chem. Int. Ed. 51 (2012)
- [4] T.J. Albrecht et al., Appl. Phys. 69, 668 (1991)
- [5] F.J. Giessibl, Appl. Phys. Lett. 73, 3956 (1998)
- [6] L. Bartels et al., Phys. Rev. Lett. 80, 2004 (1998)

O 75.10 Thu 18:15 H38

Force and conductance of contacts to a C₆₀ molecule — •NADINE HAUPTMANN¹, FABIAN MOHN², LEO GROSS², GERHARD MEYER², THOMAS FREDERIKSEN³, and RICHARD BERNDT¹ — ¹Institut für Exp. und Angew. Physik der Universität Kiel (IEAP), D-24098 Kiel, Germany — ²IBM Research - Zurich, 8803 Rüschlikon, Switzerland — ³Donostia International Physics Center (DIPC), E-20018 Donostia-San Sebastián, Spain

When a single molecule is contacted to measure its conductance new bonds are formed and significant forces may arise. These forces affect the atomic-scale junction geometry, which is crucial for its transport properties. We present simultaneously measured low-temperature force and conductance data from controlled Cu-C₆₀ and C₆₀-C₆₀ contacts with submolecular resolution. The contact conductances reported in prior works are shown to correspond to the junction being under maximal tensile stress. In order to estimate relaxations we fit the calculated conductance for a rigid system to the experimental data considering an effective spring constant for the molecular junction. The results indicate that most of the deformation in a Cu-C₆₀ contact may be ascribed to relaxations of the Cu tip.

O 75.11 Thu 18:30 H38

Simulation of C₆₀ non-equilibrium surface growth — •NICOLA KLEPPMANN¹, SEBASTIAN BOMMEL^{2,3}, STEFAN KOWARIK³, and SABINE H. L. KLAPP¹ — ¹Institut für Theoretische Physik, Technische Universität Berlin, Hardenbergstr. 36, 10623 Berlin, Germany — ²Deutsches Elektronen-Synchrotron (DESY), Notkestr. 85, 22607 Hamburg, Germany — ³Institut für Physik, Humboldt-Universität zu Berlin, Newtonstr. 15, 12489 Berlin, Germany

Kinetic Monte Carlo simulation methods allow the simulation of non-equilibrium epitaxial surface growth over experimentally realized time spans of minutes and growth of multiple layers of particles [1]. Through variation of simulated temperature and adsorption rate the structures formed can be manipulated and predictions for experimental methods such as molecular beam epitaxy can be made. We apply the method to simulate multilayer growth of C₆₀. The material parameters are obtained through comparison with Grazing-Incidence X-ray Scattering measurements [2]. The simulations allow for a time-resolved analysis of the real and reciprocal surface, geometric and statistical analysis as well as an understanding of microscopic processes obtained from particle trajectories. Characteristic time-dependent features such as the average island distance and layer filling fraction are consistent with the experimental data for long time spans and several temperatures.

[1] A. Chatterjee and D. G. Vlachos, J. Comp.-Aided Mater. Des. 14, 253-308 (2007)

[2] S. Kowarik, A. Gerlach, S. Sellner, F. Schreiber, L. Cavalcanti and O. Konovalov, Phys. Rev. Lett. 96, 125504 (2006)

O 75.12 Thu 18:45 H38

Adsorption site determination of a molecular monolayer via inelastic tunneling — •DANIEL WEGNER^{1,2}, RYAN YAMACHIKA², XIAOWEI ZHANG², YAYU WANG², MICHAEL F. CROMMIE², and NICOLÁS LORENTE³ — ¹Physikalisches Institut und CeNTech, Westfälische Wilhelms-Universität Münster, 48149 Münster, Germany — ²University of California at Berkeley and Lawrence Berkeley National Laboratory, Berkeley, California 94720-7300, USA — ³Centre d'Investigació en Nanociència i Nanotecnologia, CIN2 (CSIC-ICN), 08193 Bellaterra, Spain

We have combined scanning tunneling microscopy (STM) with inelastic electron tunneling spectroscopy (IETS) and density functional theory (DFT) to study a tetracyanoethylene (TCNE) monolayer on Ag(100). Images show that the molecules arrange in locally ordered patterns with three non-equivalent, but undeterminable, adsorption sites. While scanning tunneling spectroscopy (STS) only shows subtle variations of the local electronic structure at the three different positions, we find that vibrational modes are very sensitive to the local atomic environment. IETS detects sizeable mode frequency shifts of the molecules located at the three topographically detected sites, which permits us to determine the molecular adsorption sites through identification with DFT calculations. This proof-of-principle study shows

that IETS combined with DFT can be used to discriminate between non-equivalent molecular adsorption environments in a dense complex molecular monolayer that lacks long-range order and thus would be challenging to study using diffraction-based techniques.

O 75.13 Thu 19:00 H38

Chemisorbed Monolayers of Corannulene Penta-Thioethers on Gold — •POLINA ANGELOVA¹, EPHRATH SOLEL², GALIT PARVARI², ANDREY TURCHANIN¹, MARK BOTOSHANSKY², EHUD KEINAN², and ARMIN GÖLZHÄUSER¹ — ¹Physics of Supramolecular Systems and Surfaces, University of Bielefeld, Germany, — ²Schulich Faculty of Chemistry, Technion - Israel Institute of Technology, Haifa

32000, Israel

Corannulene pentathioethers form highly stable monolayers on gold surfaces, as indicated by X-ray photoelectron spectroscopy (XPS). Formation of these homogeneous monolayers involves multivalent coordination of the five sulfur atoms to gold with the peripheral alkyl or aryl substituents pointing away from the surface. No dissociation of C-S bonds upon binding could be observed at room temperature. The XPS experiments reveal strong chemical bonding between the thioether groups and gold, comparable to the bonding between thiolates and gold surfaces. Temperature-dependent XPS study shows that the thermal stability of the monolayers is higher than the typical stability of self-assembled monolayers (SAMs) of thiolates on gold.