

## O 14: Organic/bio Molecules on Metal Surfaces II

Time: Monday 16:00–19:00

Location: TRE Phy

O 14.1 Mon 16:00 TRE Phy

**Adsorption behavior of porphycenes on a Cu(111) surface: A scanning tunneling microscopy study** — ●MICHAEL STARK, STEFANIE DITZE, MICHAEL LEPPER, JOHANNES TRÄG, LIANG ZHANG, 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

The knowledge of the adsorption behavior of large organic molecules, like porphyrin derivatives, on surfaces is a prerequisite to engineer their supramolecular architecture and to finally utilize their functional properties. Herein, we expand the surface science studies of porphyrins to their constitutional isomers, the so-called porphycenes. We investigate 2H-2,7,12,17-tetraphenylporphycene (2HTPPc) and 2H-2,7,12,17-tetrakis-(4-tert-butyl)-phenylporphycene (2HTTBPPc) on Cu(111) with scanning tunneling microscopy (STM) under ultra-high vacuum (UHV) conditions. Thereby, we found a dominant registry of the porphycene core with the substrate, regardless of its peripheral substituents and the actual supramolecular structures formed. Different supramolecular structures were identified depending on the peripheral substituents of the porphycenes. A particular interesting behavior is observed for 2HTPPc which assembles in highly ordered rows separated by rather loosely arranged molecular rows. In the latter we also observe occasional rotation of individual molecules at room temperature. The results will be presented and discussed addressing the role of specific molecule-molecule interactions.

O 14.2 Mon 16:15 TRE Phy

**Interplay of hydrogen bonding and molecule-substrate interaction in self-assembled adlayer structures of tetra(*p*-hydroxyphenyl)porphyrin on Ag(110)** — ●LARS SMYKALLA<sup>1</sup>, PAVEL SHUKRYNAU<sup>1</sup>, MICHAEL HIETSCHOLD<sup>1</sup>, CAROLA MENDE<sup>2</sup>, and HEINRICH LANG<sup>2</sup> — <sup>1</sup>Technische Universität Chemnitz, Institute of Physics, Solid Surfaces Analysis Group, D-09107 Chemnitz, Germany — <sup>2</sup>Technische Universität Chemnitz, Institute of Chemistry, Inorganic Chemistry, D-09107 Chemnitz, Germany

The construction of desired molecular architectures on surfaces can be achieved by the self-assembly of molecular building blocks. The arrangement of adsorbed molecules is mainly controlled by a complex interplay between intermolecular interactions, such as hydrogen bonds, dispersion and electrostatic interactions, and the molecule-substrate interaction, that is the adsorption on favourable positions on the substrate lattice. We report on the adsorption and self-organisation of 5,10,15,20-tetra(*p*-hydroxyphenyl)porphyrin molecules on the highly anisotropic Ag(110) surface. One-dimensional molecular chains as well as three molecular structures with large unit cells, each containing a different number of molecules, were observed using scanning tunnelling microscopy. The molecules in the arrangements form hydrogen bonds and, additionally, show  $\pi$ - $\pi$  stacking of phenyl-groups. The difference between the unit cells is the number of hydrogen bonds per molecule and correspondingly a different epitaxy. Density Functional Theory calculations are presented to explain the complex adsorption and epitaxial behaviour of these molecules on Ag(110) in detail.

O 14.3 Mon 16:30 TRE Phy

**Fabrication of chemical templates for the selective adsorption of functional molecules by Focused Electron Beam Induced Processing** — ●MARTIN DROST, FAN TU, ESTHER CARRASCO, FLORIAN VOLLNHALS, HANS-PETER STEINRÜCK, and HUBERTUS MARBACH — Lehrstuhl für Physikalische Chemie II, Universität Erlangen-Nürnberg, Egerlandstr. 3, D-91058

The fabrication of well-defined nanostructures is usually realized by choosing one of the two main methods: the bottom-up approach, e.g. the self-assembly of supramolecular structures on surfaces, and top-down methods like electron beam lithography. We target at combining both methods such that local surface modifications by focused electron beam induced processing (FEBIP) act as a template for the adsorption of functional molecules, here 2H-Tetraphenylporphyrin (2HTPP). First, the adsorption behavior of 2HTPP on metal surfaces like Cu(111) and Rh(110) with and without adsorbed oxygen was studied. Second, the feasibility of locally altering the surface by FEBIP, e.g. by local electron induced oxygen desorption for the directed adsorp-

tion of 2HTPP, was investigated by a combination of Scanning Electron Microscopy (SEM), Auger Electron Spectroscopy (AES) and Scanning Tunneling Microscopy (STM). Latest results will be presented and discussed.

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O 14.4 Mon 16:45 TRE Phy

**Adsorption geometry and intramolecular conformation of Ni(II)-tetraphenyl-benzoporphyrin on Cu(111)** — ●LIANG ZHANG, MICHAEL LEPPER, MICHAEL STARK, STEFANIE DITZE, 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

Self-assembly of molecular building blocks on well-defined surfaces by supramolecular coordination provides a promising approach for the bottom-up fabrication of two-dimensional nanostructures with outstanding properties. In this respect, porphyrins are particularly attractive because of their distinct chemical and physical properties.

In this presentation, we expand our scanning tunneling microscopy studies to the adsorption of Ni(II)-tetraphenyl-benzoporphyrin (NiTPBP) on Cu(111) under ultra-high vacuum (UHV) conditions, mainly at room temperature (RT). NiTPBP shows a peculiar interesting adsorption behavior with coexisting domains of different supramolecular structure and individual molecules exhibiting deviant orientation within a particular supramolecular arrangement. The observed supramolecular assemblies, the corresponding intermolecular interactions and the dynamic behavior of the molecules will be discussed in detail.

O 14.5 Mon 17:00 TRE Phy

**Controlling intramolecular hydrogen transfer** — ●TAKASHI KUMAGAI<sup>1</sup>, FELIX HANKE<sup>2</sup>, SYLWESTER GAWINKOWSKI<sup>3</sup>, JOHN SHARP<sup>2</sup>, KONSTANTINOS KOTSIS<sup>2</sup>, JACEK WALIK<sup>3</sup>, MATS PERSSON<sup>2,4</sup>, and LEONHARD GRILL<sup>1,5</sup> — <sup>1</sup>Fritz-Haber Institute, Berlin, Germany — <sup>2</sup>University of Liverpool, Liverpool, UK — <sup>3</sup>Polish Academy of Science, Warsaw, Poland — <sup>4</sup>Chalmers University of Technology, Göteborg, Sweden — <sup>5</sup>University of Graz, Graz, Austria

Although the local environment of a molecule can play an important role in its chemistry, rarely has it been examined experimentally at the level of individual molecules. We report the precise control of intramolecular hydrogen transfer reactions (i.e. tautomerization) in single porphycene molecules using low-temperature scanning tunneling microscopy (STM) [1]. Single porphycene molecules adsorbed on a Cu(110) surface were imaged by STM at 5 K and found to have only cis configuration in which the inner H-atoms located on the one side in the cavity. The cis-cis tautomerization is induced either by STM via inelastic electron tunneling process at 5 K or thermal activation at elevated temperatures. We found that the tautomerization can be precisely tuned up and down by placing a Cu adatom nearby a molecule. The adatom is controlled using the STM manipulation.

[1] T. Kumagai et al. Nature Chemistry, accepted.

O 14.6 Mon 17:15 TRE Phy

**Copper Phthalocyanine Monolayers and Multilayers on Ag(110) and Ag(111) surfaces** — ●KATHRIN SCHÖNAUER<sup>1,2</sup>, MARTIN WILLENBOCKEL<sup>1,2</sup>, BENJAMIN STADTMÜLLER<sup>1,2</sup>, CHRISTIAN KUMPF<sup>1,2</sup>, SERGEY SOUBATCH<sup>1,2</sup>, and STEFAN TAUTZ<sup>1,2</sup> — <sup>1</sup>Peter Grünberg Institut (PGI-3), Forschungszentrum Jülich, 52425 Jülich, Germany — <sup>2</sup>JARA - Fundamentals of Future Information Technology, Germany

Organic semiconductors and their potential for applications in electronic devices such as solar cells and organic light emitting diodes make them interesting for fundamental research. Especially interfaces between different organic layers, e.g. PTCDA and CuPc, are subjects of experiments. To create a basis for the understanding of heteroorganic systems, the corresponding homomolecular phases are investigated regarding their geometric and electronic structure upon adsorption on a metal surface. While homomolecular phases of PTCDA on different noble metal surfaces are well-studied, less is known about adsorption and ordering of CuPc. Here we present a combined study employing

(SPA)LEED, STM, STS and ARUPS to CuPc monolayers and multilayers adsorbed on the Ag(110) and Ag(111) surfaces.

O 14.7 Mon 17:30 TRE Phy

**Charged adsorbates among each other: Simulating intermolecular interactions of free-base porphine on coinage metal surfaces** — ●MORITZ MÜLLER, REINHARD J. MAURER, KATHARINA DILLER, and KARSTEN REUTER — Technische Universität München

Designed through the process of evolution, porphine naturally serves as a basic unit in heme proteins and chlorophyll. Functionality and robustness of these compounds suggest potential applications tackling photovoltaics, nano-catalysis, data storage, and drug design. Many technical realizations require controllable surface engineered coating of ordered molecular films on two-dimensional boundaries. Adsorbed to coinage metal surfaces, porphine overlayers exhibit a variety of different superstructures [1], depending on the coverage. We report modeling of free-base porphine on clean Ag(111) and Cu(111) surfaces in the framework of dispersion-corrected semi-local Density Functional Theory. The lateral interactions determining the overlayer structure can be expressed as two competing forces: attractive van-der-Waals interactions and repulsive electrostatic interactions between the charge-transfer-induced adsorbate dipoles. Our investigations of the adsorption geometries and the electronic structure display, in agreement with experiment, a substantial amount of charge-transfer to the molecule upon adsorption. Based on our *ab-initio* calculations a simple interaction model is introduced and corresponding conclusions are drawn towards the coverage-dependent supermolecular arrangement and the effects of adsorbate functionalization.

[1] F. Bischoff *et al.*, ACS Nano, **7**, 3139 (2013)

O 14.8 Mon 17:45 TRE Phy

**Chiral Conflict among Different Helicenes Suppresses Formation of One Enantiomorph in 2D Crystallization** — ●JOHANNES SEIBEL<sup>1</sup>, OLIVER ALLEMANN<sup>2</sup>, JAY S. SIEGEL<sup>2</sup>, and KARL-HEINZ ERNST<sup>1,2</sup> — <sup>1</sup>Empa, Swiss Federal Laboratories for Materials Science and Technology, 8600 Dübendorf, Switzerland — <sup>2</sup>Department of Chemistry, University of Zürich, 8057 Zürich, Switzerland

Intermolecular chiral recognition plays a key role in the spontaneous resolution of enantiomers in crystallization or diastereomeric salt crystallization, a common technique for enantiomer separation in industry. Diastereomeric interactions in 2D crystals formed at solid surfaces serve as excellent models to study the underlying molecular recognition processes, where scanning tunneling microscopy provides submolecular resolution. The adsorption of a [5,6,9,10]-dibenzopentahelicene (db[5]H) racemate on Au(111) leads to 2D conglomerate formation, i. e. homochiral mirror domains containing only one enantiomer are observed, which is in contrast to previous results obtained for [7]H on Cu(111). Upon mixing M-[7]H into the monolayer, the balance between the mirror domains shifts gradually, until only the P-db[5]H enantiomorph is left in a monolayer containing 26% M-[7]H. This is explained by a preferred diastereomeric interaction between different helicene species of opposite handedness, suppressing the formation of the pure P-db[5]H enantiomorph by capturing P-db[5]H in non-ordered areas. These results show that dispersive forces can act in a manner comparable to polar forces in chiral discrimination at surfaces.

O 14.9 Mon 18:00 TRE Phy

**Effect of crystal packing on the electronic properties of free base porphyrins** — ●MARGHERITA MARSILI<sup>1</sup>, PAOLO UMARI<sup>1</sup>, ANDREA GOLDONI<sup>2</sup>, and MADDALENA PEDIO<sup>3</sup> — <sup>1</sup>Dipartimento di Fisica - Università di Padova - 35131 Padova Italy — <sup>2</sup>Sincrotrone Trieste, Area Science Park, 34149 Basovizza, Trieste Italy — <sup>3</sup>IOM-CNR, TASC Area Science Park Bul., 34149 Basovizza, Trieste, Italy

Porphyrins, a group of organic aromatic molecules, are involved in important biological processes such as oxygen transfer in red blood cells, or light harvesting in plants. Similar functions can be exploited in artificial devices, therefore the understanding and control of their electronic properties is of great interest.

In this work we present the combined theoretical and experimental study of metal free H2OEP and H2TPP, addressing the electronic properties from single molecule to molecular solids. Thin films have been investigated combining valence band photoemission, inverse photoemission spectroscopy and XAS, and the results compared with isolated molecule gas phase spectra and state-of-the-art GW calculations.

O 14.10 Mon 18:15 TRE Phy

**From Benzenetrithiolate Self-Assembly to Copper-Sulfide**

**Adlayers on Cu(111): Temperature-Induced Irreversible and Reversible Phase Transitions** — THOMAS SIRT<sup>1,2</sup>, ●MATTHIAS LISCHKA<sup>1,2</sup>, ATENA RASTGOO-LAHROOD<sup>1,2</sup>, JOHANNA EICHHORN<sup>1,2</sup>, THOMAS STRUNSKUS<sup>3</sup>, WOLFGANG M. HECKL<sup>1,2,4</sup>, and MARKUS LACKINGER<sup>1,2,4</sup> — <sup>1</sup>Department of Physics, Technische Universität München, James-Frank-Str. 1, 85748 Garching — <sup>2</sup>Center for NanoScience (CeNS), Schellingstr. 4, 80799 Munich — <sup>3</sup>Institute for Materials Science - Multicomponent Materials, Christian-Albrechts-Universität zu Kiel, Kaiserstr. 2, 24143 Kiel — <sup>4</sup>Deutsches Museum, Museumsinsel 1, 80538 Munich (all Germany)

Self-assembly and thermally activated surface chemistry of 1,3,5-benzenetrithiol on Cu(111) are studied under ultrahigh vacuum conditions. Low energy electron diffraction patterns acquired at room temperature and during subsequent heating reveal irreversible and reversible phase transitions between in total four different long-range ordered phases. X-ray photoelectron spectroscopy of the different phases facilitates to identify major chemical changes for the phase transitions. The structural characterization of each phase is carried out by high resolution scanning tunneling microscopy and adsorption geometries of the phenyl rings are derived from C 1s near edge x-ray absorption fine structure. Combination of the results from this array of experimental techniques leads to a consistent picture from benzene thiolate monolayer to copper sulfide superstructures and underlying processes.

O 14.11 Mon 18:30 TRE Phy

**Structural phase dynamics and intermolecular coupling studied by energy-dispersive NEXAFS** — ●MARKUS SCHOLZ<sup>1,2,3</sup>, CHRISTOPH SAUER<sup>1,2</sup>, MICHAEL WIESSNER<sup>1,2</sup>, THAN-NAM NGUYEN<sup>1,2</sup>, ACHIM SCHÖLL<sup>1,2</sup>, and FRIEDRICH REINERT<sup>1,2</sup> — <sup>1</sup>Universität Würzburg, Experimentelle Physik VII, Am Hubland, D-97074 Würzburg — <sup>2</sup>Karlsruher Institut für Technologie (KIT), Gemeinschaftslabor für Nanoanalytik, D-76021 Karlsruhe — <sup>3</sup>Present address: Institut für Experimentalphysik, Universität Hamburg, Luruper Chaussee 149, D-22761 Hamburg

We study the formation of a 3D geometric structure in molecular films, which emerges from an initially amorphous layer by the means of energy-dispersive near edge x-ray absorption fine-structure spectroscopy. This novel technique allows NEXAFS experiments with full spectroscopic information on the time scale of seconds. On the example of NTCDA multilayer films, we identify several sub-processes involved in the structure formation and quantify thermodynamic parameters [1]. In a particular transient phase, which exists only for several minutes during the structure formation, we observe peculiar changes of the line shape and energy position of the C K-NEXAFS signal with respect to the bulk and gas phase spectra. By a comparison to a theoretical model based on a coupling of transition dipoles, which is established for optical absorption, we demonstrate that the observed spectroscopic differences can be explained by an intermolecular delocalized core hole-electron pair [2]. [1] M. Scholz *et al.*, New J. Phys. **15**, 083052 (2013). [2] M. Scholz *et al.*, Phys. Rev. Lett. **111**, 048102 (2013).

O 14.12 Mon 18:45 TRE Phy

**Self-assembly of de-novo synthesized functionalized pyrenes on coinage metal surfaces** — ●TOBIAS KAPOSI<sup>1</sup>, SUSHOBHAN JOSHI<sup>1</sup>, TOBIAS HOH<sup>1</sup>, ALISSA WIENGARTEN<sup>1</sup>, TOMAS MARANGONI<sup>2</sup>, DAVIDE BONIFAZI<sup>2,3</sup>, KNUD SEUFERT<sup>1</sup>, DAVID ÉCICJA FERNÁNDEZ<sup>1</sup>, WILLI AUWÄRTER<sup>1</sup>, and JOHANNES V. BARTH<sup>1</sup> — <sup>1</sup>Physik Department E20, Technische Universität München, Garching, Germany — <sup>2</sup>Dipartimento di Scienze Chimiche e Farmaceutiche and UdR INSTM, Università di Trieste, Trieste, Italy — <sup>3</sup>Department of Chemistry and Namur Research College, University of Namur, Namur, Belgium

Supramolecular architectures on metallic surfaces provide multiple prospects for the engineering of novel nanostructured materials. Of particular interest are building blocks with inherent functional properties, such as single molecule magnets or photoactive groups.

Here we report a scanning tunneling microscopy study on the self-assembly of a family of pyridil- and phenyl-functionalized pyrenes, including an optically active backbone molecule already used in commercial dyes, on Ag(111) and Cu(111). By systematically changing the molecular functionalization and symmetry, different supramolecular synthons are expressed. Phenyl-substituents result in a uniform pyrene distribution on the surface, whereas pyridil-terminations drive the formation of different regular 2D networks, that may surprisingly include metal-organic binding motifs engaging Ag adatoms. The electronic features of these systems were probed by scanning tunneling spectroscopy.