

O 64: Metal Substrates: Adsorption of Organic/Bio Molecules IV

Time: Thursday 11:15–12:45

Location: HE 101

O 64.1 Thu 11:15 HE 101

Molecular Recognition on Surfaces: Controlling Dimensionality and Periodicity of Supramolecular Tetraarylporphyrin Assemblies by the Interplay of Cyano and Alkoxy Substituents — ●NIKOLAI WINTJES¹, JENS HORNING², JORGE LOBO-CHECA¹, TOBIAS VOIGT², TOMÁŠ SAMUELY¹, CARLO THILGEN², MEIKE STÖHR¹, FRANÇOIS DIEDERICH², and THOMAS JUNG³ — ¹Department of Physics, University of Basel, CH-4056 Basel — ²Laboratorium für Organische Chemie, ETH-Zürich, Hönggerberg, HCI, CH-8093 Zürich — ³Laboratory for Micro- and Nanotechnology, Paul Scherrer Institute, CH-5232 Villigen PSI

The self-assembly of three porphyrin derivatives was studied in detail on a Cu(111) substrate by means of Scanning Tunneling Microscopy (STM). All derivatives bear two 4-cyanophenyl substituents in opposing meso-positions of the porphyrin core but differ in the nature of the other two meso-alkoxyphenyl substituents. At coverages below 0.8 monolayers, two derivatives form molecular chains which evolve into nanoporous networks at higher coverages. The third derivative self-assembles directly into a nanoporous network without showing a one-dimensional phase. The pore-to-pore distances for the three networks depend on the size and shape of the alkoxy substituents. All observed effects are explained by (i) an interplay between the steric demand of the alkoxy residues, (ii) polar bonding involving both cyanophenyl and alkoxyphenyl substituents, and (iii) the entropy/enthalpy balance of the network formation.

O 64.2 Thu 11:30 HE 101

A structural study of porphyrins interacting with a metallic surface — ●JENS BREDE, GERMAR HOFFMANN, and ROLAND WIESEN-DANGER — Institut of Applied, University of Hamburg

A Porphyrin is a heterocyclic macrocycle derived from pyrrolic subunits interconnected via methine bridges. Porphyrins are an ubiquitous class of naturally occurring compounds with important biological representatives including hemes and chlorophylls. We prepared various tetra phenyl porphyrins (TPP) with different central metal (M) ions on metallic substrates. The molecular systems were investigated by scanning tunnelling microscopy and spectroscopy. The experiments were performed in a home-built low temperature STM working at 6 K in ultra-high vacuum conditions. Upon deposition of porphyrins on metal substrates the aromatic core of the molecule may undergo a structural deformation depending on the details of the molecule-substrate interaction. We will discuss the structural conformation of TPPs and their electronic properties.

O 64.3 Thu 11:45 HE 101

Ordering Aspects of Porphyrin Derivates on Ag(111) — ●HUBERTUS MARBACH, FLORIAN BUCHNER, KARMEN COMANICI, and HANS-PETER STEINRÜCK — Universität Erlangen-Nürnberg, Lehrstuhl für Physikalische Chemie II, D-91058 Erlangen

Porphyrins appear to be ideal candidates to generate functional molecular devices, due to their self assembly properties and their versatile functionality. In the present contribution, we focus on general aspects of ordered phases of different porphyrin derivates in the monolayer regime on Ag(111) investigated by STM. Tetraphenylporphyrins (TPP) always appear to arrange themselves in a square configuration, with a lattice constant of 1.4 nm at RT, independent of the central metal ion. Micrographs with submolecular resolution reveal the details of the molecular arrangement and allow to identify a "T-type" intermolecular interaction in between the phenyl substituents as the main reason for the observed ordering. Interestingly, the TPP molecules tend to rearrange upon exposure to large doses of small molecules (e.g., NO), which is interpreted as due to coadsorption of the dosed molecules. In contrast to TPP, the more bulky Tetrakis-(3,5-di-tert-butyl)-phenyl porphyrins (TTBPP) exhibit different coexisting phases. An specific route to prepare a monolayer, namely the thermal desorption of excess multilayers, leads to an extremely stable CoTTBPP layer, due to a highly interwoven structure. The role of intermolecular and intramolecular interactions and adsorbate/substrate interactions in respect to the observed phases and 2D-chirality aspects will be discussed. This work has been funded by Sonderforschungsbereich 583.

O 64.4 Thu 12:00 HE 101

Formation, electronic structure, and reactivity of adsorbed metalloporphyrin complexes — ●J. MICHAEL GOTTFRIED, KEN FLECHTNER, YUN BAI, ANDREAS KRETSCHMANN, MARIE-MADELEINE WALZ, ANDREAS BAYER, and HANS-PETER STEINRÜCK — Universität Erlangen-Nürnberg, Lehrstuhl für Physikalische Chemie II

Supported metal complexes are promising candidates for novel, regularly nanostructured catalysts. The coordinated metal centers represent well-defined active sites, which are immobilized by anchoring the ligands to a solid surface. Thus, these systems combine the advantages of homogeneous and heterogeneous catalysts. To develop a fundamental understanding of their functional principles, we have studied the formation, the electronic structure, and the reactivity of various porphyrin-based metal complexes on Ag(111) using photoelectron spectroscopy and complementary techniques. Specifically, we will discuss the axial coordination of NO on adsorbed Co(II)-tetraphenylporphyrin (CoTPP) and the influence of this ligand on the electronic interaction between the Co ion and the underlying Ag surface.¹ In addition, the formation of the complex H₃N-ZnTPP (by reaction between tetraphenylporphyrin, Zn, and NH₃ on an Ag(111) surface) will be used to illustrate a novel two-step route for the in-situ synthesis of adsorbed metalloporphyrin complexes.² — Supported by the DFG through SFB 583. — [1] K. Flechtner, A. Kretschmann, H.-P. Steinrück, J.M. Gottfried, *J. Am. Chem. Soc.* 129 (2007) 12110. — [2] K. Flechtner, A. Kretschmann, L.R. Bradshaw, M.M. Walz, H.-P. Steinrück, J.M. Gottfried, *J. Phys. Chem. C* 111 (2007) 5821.

O 64.5 Thu 12:15 HE 101

Voltage-dependent contrast of Co-Tetraphenylporphyrin Molecules on Ag(111) — ●FLORIAN BUCHNER, KARMEN COMANICI, KEN FLECHTNER, THOMAS LUKASCZYK, J. MICHAEL GOTTFRIED, HUBERTUS MARBACH, and HANS-PETER STEINRÜCK — Lehrstuhl für Physikalische Chemie II, Universität Erlangen-Nürnberg, Egerlandstr. 3, 91058 Erlangen

The self-assembly of molecules on single-crystal surfaces is an approach towards the creation of novel materials with outstanding properties. Porphyrins represent a group of molecules which are of great interest for applications as well as for fundamental research. In this contribution, it will be shown that the appearance of tetraphenylporphyrins (TPP) in scanning tunneling microscopy (STM) topographs strongly depends on the applied bias voltage. Here we report the observation and identification of certain features in STM images of CoTPP layers on Ag(111). A significant portion of an ordered monolayer of CoTPP appears as depression at bias voltages around -1 V. At reduced negative bias voltages, the contrast of the depressions fade and at bias voltages around +1 V, the contrast is inverted. Investigating the electronic structure of CoTPP and 2HTPP layers by means of ultraviolet photoelectron spectroscopy (UPS) and scanning tunneling spectroscopy (STS), the contrast mechanism could be clarified, enabling us to interpret the depressions as 2HTPP. Additional evidence could be provided by imaging layers of different mixtures and by high-resolution STM images of the features in CoTPP. This work has been funded by the DFG through Sonderforschungsbereich 583.

O 64.6 Thu 12:30 HE 101

Conformational study of FeTPC molecules on Cu(111) with STM — ●STEFAN KUCK, GERMAR HOFFMANN, and ROLAND WIESEN-DANGER — Institute of Applied Physics, Jungiusstr. 9a, 20355 Hamburg

When porphyrin molecules are studied on surfaces, an important issue is the conformation of the molecule. So far, it was not possible to determine with STM whether the molecules are in a saddle or in a planar geometry. To answer this question, we introduce corroles as a new class of molecules in the field of STM studies, which are related to porphyrins but with reduced symmetry. Here, we address Iron-Triphenyl Corrole (FeTPC) molecules deposited on the Cu(111) surface with scanning tunneling microscopy. We will discuss the bending of the corrole core into the saddle conformation and the configuration of the phenyl legs in contact with the metallic substrate.