A structural study of porphyrins interacting with a metallic surface — J. Jens Brede, Germar Hoffmann, and Roland Wiesen-danger — Institut of Applied, University of Hamburg

A porphyrin is a heterocyclic macrocycle derived from pyrrole sub-units 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.

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, 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.


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.