O 85: Metal substrates: Adsorption of organic / bio molecules VII

Time: Friday 11:15–13:00 Location: H36

O 85.1 Fri 11:15 H36

Thin films and monolayers of metalloporphyrines and -phthalocyanines: Examination of the reactive sites — •Martin Schmid, Yun Bai, Michael Sekita, Hans-Peter Steinrück, and J. Michael Gottfried — Universität Erlangen-Nürnberg, Lehrstuhl für Physikalische Chemie II, Egerlandstr. 3, 91058 Erlangen, Germany

Planar metal complexes such as metalloporphyrins and -phthalocyanines show various chemical and structural properties that make them promising candidates for many technological purposes, ranging from gas sensors and catalytic applications to molecular electronic devices. In the absence of axial ligands, those complexes possess coordinatively unsaturated central metal ions which then play a key role as reactive and/or coordinative sites. For a detailed mechanistic understanding of the electronic interactions, especially at the central metal ion, we prepared thin films and monolayers of Co, Fe and Cu porphyrines and -phthalocyanines under ultrahigh vacuum conditions on Ag(111) and Au(111) single crystal surfaces. The systems were analyzed by UV and X-ray photoelectron spectroscopy; these methods are sensitive to the valence electronic structure of the interface and to the oxidation states of the metal centers, respectively. Our investigations revealed that changes in the chemical environment, e.g., by coordination of small reactive molecules such as O_2 and CO, as well as subtle differences in the molecular geometry, the nature of the substrate, and even temperature variations can alter the oxidation state of the metal center and the character of its interaction with the substrate.

O 85.2 Fri 11:30 H36

Complex nanoporous networks from flexible functionalised porphyrin units — •David Écija[1], Knud Seufert[1], Willi Auwärter[1], Claudia Aurisicchio[2], Davide Bonifazi[2], Daniel Heim[1], and Johannes V. Barth[1] — [1]Physik Department, E20, Technische Universität München, James-Franck Str. 1, D-85748 Garching, Germany — [2]Department of Chemistry, University of Namur, Rue de Bruxelles 61, B-5000 Namur, Belgium

Porous materials are attracting wide interest because of the presence of cavities, which can selectively accomodate guest species. Here we report on a low temperature STM study of the formation of two different bidimensional supramolecular porous networks made of trans- and cis-like porphyrin derivatives on Ag(111) in ultra high vacuum. In either case, there is a high level of homogeneity in the pore size, shape and chemical composition, as required for applications. The trans-like porphyrin self-assembles into a hexagonal porous network, with an inter-pore distance of 5.3 nm and a pore area of 0.9 nm2. Chirality plays a major role, giving as a result two different domains, each of them made of only one kind of enantiomer. The cis-like species self-assembles into a Kagomé porous network, with an interpore distance of 4.8 nm and a pore area of 0.28 nm2.

Due to the donor character of the molecular species involved, on going experiments are focused on the deposition of acceptor molecules on top of the porous templates, with the idea of improving the efficiency of new kind of organic solar cells.

O 85.3 Fri 11:45 H36

Strategies to fabricate molecular architectures by local anchoring and functionalization of porphyrins — Florian Buchner, Elisabeth Zillner, Michael Röckert, Stefanie Glässel, Hans-Peter Steinrück, and •Hubertus Marbach — Lehrstuhl für Physikalische Chemie II and Interdisciplinary Center for Molecular Materials (ICMM), Friedrich-Alexander-University Erlangen-Nuremberg, Egerlandstr. 3, 91058 Erlangen

For the generation of functional molecular devices the ultimate goal is the control of the position, supramolecular arrangement, intramolecular conformation and electronic coupling of the molecular building blocks to the substrate. Porphyrins appear to be ideal building blocks to generate such devices on surfaces, since they combine an active site, usually a coordinated metal center, with a planar, structure forming element. In this contribution we discuss scanning tunneling microscopy (STM) investigations of the dynamics, supramolecular ordering and intramolecular conformation of different porphyrins on Ag(111), Cu(111) and composite surfaces in ultra-high vacuum, mainly at room temperature. The presented data enables the understanding of the role of molecule-molecule and molecule-substrate interactions. The obtained findings indicate the possibility to locally anchor and/or functionalize (e.g. metalate) the porphyrins on surfaces prestructured with metallic or oxygen islands. Based on these results a technique for large scale patterning with the corresponding molecules will be proposed. This work has been funded by the DFG through Sonderforschungsbereich 583.

O 85.4 Fri 12:00 H36

Combined STM and theoretical first-principles study of ligated metalloporphyrins adsorbed on noble metal surfaces — •Knud Seufert[1], Willi Auwärter[1], Marie-Laure Bocquet[2], Nicolas Lorente[3], Alexander Weber-Bargioni[4], Joachim Reichert[1,4], and Johannes V. Barth[1] — [1]Physik Department, E20, Technische Universität München, Garching, Germany — [2]Laboratoire de Chimie, ENS, Lyon, France — [3]CIN2, Barcelona, Spain — [4]Physics Department, University of British Columbia, Vancouver, Canada

Motivated by the importance of metalloporphyrins in many biological processes, such as the transport of respiratory gases, we present a combined experimental and theoretical study of the interaction of gaseous ligands with porphyrins. The metalloporphyrins (M-TPP, M=Fe, Co) were anchored on Ag(111) and Cu(111) surfaces and exposed to small amounts of CO and NO. Based on low-temperature STM experiments, we discuss the M-TPP's appearance and electronic structure dependent on the additional ligand. On both surfaces, bare M-TPPs show an occupied electronic state (HOMO) and an ant-like topographic appearance, which is completely modified through the attachment of NO. The dosage of CO instead yields no drastic changes in the low-energy electronic structure of the porphyrin host.

Our theoretical investigations focus on the well defined Co-TPP/Cu(111) system. The results show that the CO is not exclusively bound to the metal center, but rather to bridge-like positions between the central metal ion and the nitrogen of the porphyrin macrocycle.

O 85.5 Fri 12:15 H36

Conformational switching of porphyrin derivatives on Au(111) by heating and STM manipulation — •Johannes Mielke[1,2], Matthew Dyer[3], Mats Persson[3], Stefan Hecht[4], Jesús Martinez-Blanco[2], Karsten Horn[2], and Leonhard Grill[1,2] — [1]Institut für Experimentalphysik, Freie Universität Berlin — [2]Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin — [3]Department of Chemistry, University of Liverpool, United Kingdom — [4]Institut für Chemie, Humboldt-Universität zu Berlin

Molecular switches, which exhibit at least two stable states with characteristic properties, could play an important role in future applications of molecular electronics for the control of the conductance or the implementation of logic functions. Although such molecules have been investigated intensely in solution, the knowledge about their switching properties when being adsorbed on a solid surface is still scarce. We have studied functionalised porphyrin molecules on a Au(111) surface at different temperatures. In STM images, two stable conformations can be distinguished by their characteristic appearance. When applying voltage pulses with the STM tip to single molecules at low temperatures (around 7 K), it is possible to switch the molecules reversibly from one conformation to the other, whereas the voltage thresholds turn out to be characteristic. On the other hand, thermal switching is observed at elevated temperatures of around 300 K. The high number of switching events in the regime of thermal switching can be used to gain detailed insight in the dependence of the switching process on the atomic-scale environment of the molecule.

O 85.6 Fri 12:30 H36

modification of supramolecular binding motifs induced by substrate registry: formation of self-assembled macrocycles and chain-like patterns — •Saranyan Vijayaraghavan — Department of Physics, University of Basel, Klingelbergstrasse 82, 4056 Basel,Switzerland

The self-assembly properties of two ZnII porphyrin isomers on Cu(111) are studied at different coverage by means of an STM. Both isomers are substituted in their meso-positions by two voluminous 3,5-di(tert-butyl)phenyl and two 4*-cyanobiphenyl groups, respectively. In the trans-isomer, the two cyanobiphenyl groups are opposite to each other, whereas they are at right angle in the cis-isomer. For coverage up to one monolayer, the cis-substituted porphyrins self-assemble to form oligomeric macrocycles held together by antiparallel CN-CN dipolar interactions and CN-H-C(sp2) hydrogen bonding. Cyclic trimers and tetramers occur frequently but everything from cyclic dimers to hexamers are observed. Upon annealing of the samples at >150 C, dimeric macrocyclic structures are observed, in which the two porphyrins are bridged by Cu atoms, as CN-Cu-NC coordination bonds. LInear chains are seen at low coverages on Cu111 and densely packed structure at high coverages. Both cis- and trans-bis(4*-cyanobiphenyl)-substituted ZnII porphyrins behave very differently on Cu(111) compared to similar porphyrins on less reactive surfaces such as Au(111) and Ag(111). A very strong molecule-substrate interaction is seen on Cu(111) which dominates all observed structures.

O 85.7 Fri 12:45 H36

Surface-assisted assembly of discrete porphyrin-based cyclic supramolecules — •Daniel Heim[1], Knud Seufert[1], Willi Auwärter[1], Claudia Aurisicchio[2], Chiara Fabbro[3], Davide Bonifazi[2,3], and Johannes V. Barth[1] — [1]Physik Department, E20, Technische Universität München, James-Franck Str. 1, D-85748 Garching, Germany — [2]Department of Chemistry, University of Namur, Rue de Bruxelles 61, B-5000 Namur, Belgium — [3]Department of Pharmaceutical Sciences, University of Trieste, Piazzale Europa 1, I-34127 Trieste, Italy

We employed de novo synthesized porphyrin modules to construct discrete cyclic supramolecular architectures supported on a copper (111) surface. Hereby, porphyrin derivates exhibiting either one or two functional pyridyl recognition groups, the latter being cis-like and trans-like isomers, were applied. The programmed geometry and functionality of the molecular modules together with their conformational flexibility and substrate interaction yields symmetric discrete assemblies, including dimers and chains as well as three- to six-membered cyclic structures. The area of the molecular cavities is extended by creating bicomponent structures combining building blocks with different symmetry. All these supramolecular architectures are stabilized by Cu surface atom mediated attractive pyridyl-pyridyl interactions. The resulting strength of the intermolecular interactions allows for conformational changes of the entire assemblies by STM manipulation.