O 14: Metal substrates: Adsorption of organic / bio molecules II

Time: Monday 15:00–17:45 Location: H36

O 14.1 Mon 15:00 H36

Random 2D metal-organic string networks based on divergent coordination assembly — •Matthias Marschall[1,2], Joachim Reichert[1,2], Alexander Weber-Bargioni[2], Knud Seufert[1], Willi Auwärter[1], Svetlana Klyatskaya[3], Giorgio Zoppellaro[3], Mario Ruben[3], and Johannes V. Barth[1,2] — [1]Physik Department E20, TU München, Germany — [2]Department of Physics & Astronomy, University of British Columbia, Vancouver, Canada — [3]Institut für Nanotechnologie, Karlsruhe Institute of Technology, Germany

The molecular-level investigation of random networks becomes possible with two-dimensional supramolecular systems assembled on well-defined surfaces. Such studies allow to identify elementary structural motifs or characteristic defects and thus provide new insights into the intriguing nature of glasses and amorphous solids. Here we report a direct scanning tunneling microscopy investigation of a random metal-organic network, comprising interconnected strings and multiple ramification motifs. We employed a nonlinear prochiral ditopic linker deconvoluted in three stereoisomers upon surface confinement. Metallosupramolecular assembly was induced by codeposited cobalt atoms engaging in lateral metal-ligand interactions with the linker dicarbonitrile endgroups. The resulting complex networks are based on a library of distinct three- and fourfold Co-carbonitrile nodal coordination motifs giving rise to bifurcation or string formation. Thus the linker symmetry deconvolution and coordination multiplicity entails divergent assembly with concomitant random reticulation of the entire surface.

O 14.2 Mon 15:15 H36

On the Scalability of Supramolecular Networks - High Packing Density vs. Optimized Hydrogen Bonds in Tricarboxylic Acid Monolayers — •Jürgen F. Dienstmaier[1], Kingsuk Mahata[2], Wolfgang M. Heckl[3], Michael Schmittel[2], and Markus Lackinger[1] — [1]LMU München, Sektion Kristallographie — [2]Universität Siegen, Organische Chemie I — [3]Deutsches Museum

We present a Scanning Tunneling Microscopy (STM) based study of 1,3,5-tris[4*-carboxy(1,1*-biphenyl-4-yl)]benzene (TCBPB) monolayers at the liquid-solid interface. In analogy to smaller aromatic threefold symmetric tricarboxylic acids, this compound was aimed to yield two-dimensional nanoporous networks with large cavities. Depending on the solute concentration, three crystallographically distinct phases with pores of different size and shape were observed on graphite (001) with heptanoic acid as solvent. All three phases have the same dimer motif as basic building block in common. Yet, as opposed to other carboxylic acid assemblies, these dimers are not interconnected by O-H...O hydrogen bonds as anticipated, but by two energetically inferior C-H...O hydrogen bonds. Instead of the common head-to-head arrangement, this bonding pattern results in displaced dimers, which exhibit lower symmetry, allow for higher packing density, and give rise to chirality of all polymorphs. In accordance with studies of comparable systems, a positive correlation between solute concentration and average surface packing density is identified, which is rationalized by thermodynamic arguments.

O 14.3 Mon 15:30 H36

Simulation of short-range order in a metal-organic network — •Harry E. Hoster, Achim Breitruck, and R. Jürgen Behm — Institute of Surface Chemistry and Catalysis, Ulm University, D-89069 Ulm, Germany

Short-range order (SRO) is a common phenomenon for surfaces and adlayers, where disturbances of a periodically ordered ground state are energetically inexpensive and thus thermally accessible. It has become common to simulate SRO using Monte-Carlo approaches based on additive models for the structure relevant interactions. The necessary parameters are usually obtained from ab-initio calculations or from fitting to experimental data. In this contribution, we will demonstrate that adlayers involving large organic molecules may exhibit a SRO with many similarities to disordered two-dimensional alloys [1]. Specifically, we focus on a structure that consists of a mixture of metal-organic complexes and organic trimers distributed on a hexagonal lattice. This distribution reflects an SRO governed by hydrogen bonds between the different types of lattice occupants. We show that this SRO, which is directly observed by scanning tunneling microscopy, can be simulated using pairwise interaction energy parameters based on a simple counting of hydrogen bonds [2].

[1] A. Bergbreiter et al., *Phys.Chem.Chem.Phys.* 9, **2007**, 5127.
[2] A. Breitruck et al., *J.Phys.Chem.C Letters*, DOI: 10.1021/jp908748w.

O 14.4 Mon 15:45 H36

Thiolate based 2D Metal-Organic-Frameworks — •Georg Eder, Hermann Walch, Jürgen Dienstmaier, and Markus Lackinger — LMU Munich, Department of Earth and Environmental Sciences

Self-assembled monolayers of the organic compound 1,3,5-tris(4-mercaptophenyl)benzene on Cu(111) are studied by Scanning Tunneling Microscopy under ultrahigh vacuum conditions. The molecular structure of this threefold symmetric compound aims at the synthesis of open pore networks through symmetric interconnection via their functional groups. Thiol groups can interact via weak hydrogen bonds, whereas deprotonated thiolate groups can form covalent disulphur bridges or metal coordination bonds. After room temperature deposition on Cu(111) we observe a close packed arrangement of deprotonated molecules that do not interact directly via their functional groups. Yet, annealing the sample up to 200°C induces phase transitions which result in two distinctly different phases where molecules bond through their functional groups. Depending on the initial coverage, we observe predominance of one of these phases. In both cases molecules coordinate with metal adatoms, thereby forming S-Cu-S metal coordination bonds. Preliminary results obtained on a Ag(111) surface suggest a similar behavior. Since the thiolate metal coordination bond provides better electronic coupling than for instance carboxylate analogues, this novel type of networks is of particular interest for molecular electronics.

O 14.5 Mon 16:00 H36

Metal/SAM/Metal junctions studied from first principles — •Jan Kučera and Axel Gross — Institute for Theoretical Chemistry, Ulm University, D-89069 Ulm, Germany

There is currently a strong interest in sandwich structures made of self-assembled monolayers (SAMs) between two metal layers (M/SAM/M) because of their potential in future nanoelectronics [1]. Recently, a M/SAM/M/SAM/M “double decker” junction was realized with two 4-mercaptopyridine SAMs sandwiched between an Au electrode and Pd and Pt monolayers [2]. We have performed periodic electronic structure calculations based on density function theory (DFT) to describe various phenomena playing a role in hybrid systems such as Au/SAM, Au/SAM/Pd, and Au/SAM/Pd/SAM/Pt with the SAMs consisting of the bifunctional thioaromatics 4-aminothiophenol or 4-mercaptopyridine [1-3]. Based on the calculated local density of states (LDOS) of the metal layers, possible explanations for experimental results will be provided which show a reduced DOS at the Fermi energy [2]. In addition, the role of van der Waals forces on the structure and stability of the SAMs has been addressed by performing DFT calculations with semi-empirical corrections for dispersion effects.
[1] M. Manolova et al., Adv. Mater. **21**, 320 (2009)
[2] F. Eberle et. al., Angew. Chem., accepted for publication.
[3] J. Kučera and A. Groß, Langmuir **24**, 13985 (2008)

O 14.6 Mon 16:15 H36

Adsorption of long-chain alkanethiols on Au(111): a look from the substrate side — •Frederick Chesneau[1], Jianli Zhao[1], Cai Shen[2], Manfred Buck[2], and Michael Zharnikov[1] — [1]Angewandte Physikalische Chemie, Universität Heidelberg, Germany — [2]EaStCHEM School of Chemistry, University of St Andrews, UK

The structure of interface between a self-assembled monolayer (SAM) of alkanethiolates and the underlying Au(111) substrate is one of the greatest mysteries of surface science. To cast light on this problem, we took SAMs of hexanethiolate (HT) and dodecanethiolate (DDT) on Au(111) as test systems and studied them by a combination of synchrotron-based high resolution X-ray photoelectron spectroscopy (HRXPS) and scanning tunneling microscopy (STM). The emphasis of the HRXPS characterization was put on the Au 4f emission of the substrate, which could be decomposed into the components related to the bulk and surface. The behavior of the surface component upon the formation of HT and DDT SAMs was monitored in detail. We observed both a shift of this component and its branching into two independent emissions, which were associated with the gold atoms in the topmost layer and gold adatoms, respectively. The branching of the surface component was correlated with the lateral structure of the SAMs as determined by STM. Conclusions on the reliability of different adsorption models for these lateral structures were derived.

O 14.7 Mon 16:30 H36

Impact of the backbone on the electronic structure of SAMs on gold — •LinJun Wang[1,2], Gerold M. Rangger[3], Lorenz Romanner[4], Tomas Bučko[5], ZhongYun Ma[1], QiKai Li[1], Zhigang Shuai[1,6], Egbert Zojer[3], and Georg Heimel[7] — [1]Institute of Chemistry, Chinese Academy of Sciences, Beijing, PR China — [2]Chemistry of Novel Materials, University of Mons Hainaut, Mons, Belgium — [3]Institute of Solid State Physics, Graz University of Technology, Graz, Austria — [4]Department of Material Physics, University of Leoben, Leoben, Austria — [5]Fakultät für Physik and Center for Computational Materials Science, Universität Wien, Wien, Austria — [6]Department of Chemistry, Tsinghua University, Beijing, PR China — [7]Institut für Physik, Humboldt-Universität zu Berlin, Berlin, Germany

Modifying metal electrodes with self-assembled monolayers (SAMs) has promising applications in organic/molecular electronics. Through a comprehensive DFT study on a series of organic thiols on Au(111) surfaces, the impact of the chemical structure of the molecular backbone on the interface electronic structure is discussed. It is found that the backbone significantly impacts the alignment of the SAM conducting states relative to the metal Fermi level; for molecules with small ionization potentials, Fermi-level pinning is observed. For the workfunction modification due to SAM adsorption, the main impact of the backbone arises from its influence on the molecular orientation on the surface. The polarizability is of only minor importance as the larger molecular dipole moments achieved with more polarizable backbones are largely compensated by increased depolarization.

O 14.8 Mon 16:45 H36

Self-assembled monolayers of molecules with dithiol anchor groups: a DFT study — •Katrin Tonigold and Axel Gross — Institute for Theoretical Chemistry, Ulm University, D-89069 Ulm, Germany

Traditionally, either aliphatic or aromatic thiols are used to prepare self-assembled monolayers on gold surfaces. If both types of thiol groups are combined in the anchor group of a molecule, the size of the anchor group as well as its electronic structure are changed. Competing reactions between the two different S-atoms and the Au-surface might take place possibly leading to different surface structures.

A molecule that contains such a dithiol anchor group is 2-Mercaptomethylbenzenethiol (MMBT). In cooperation with experimentalists from the Institute of Functional Interfaces of the Karlsruhe Institute of Technology we have studied the adsorption and structure formation of MMBT on Au(111) using DFT-GGA-calculations with semi-empirical corrections for dispersion effects. IR spectra and STM images have been simulated to allow a comparison with experimental results [1]. Furthermore, the formation of surface defects upon adsorption has been addressed.

[1] X. Stammer, K. Tonigold, M. Kind, A. Groß, Ch. Wöll *et al.*, in preparation.

O 14.9 Mon 17:00 H36

STM study of fullerene molecules on alcanethiol based monolayers — •Axel Beimborn[1], Patrick Mehring[1], Daniel Weier[1,2], and Carsten Westphal[1,2] — [1]Fakultät Physik - Technische Universität Dortmund, Otto Hahn-Str. 4, D 44221 Dortmund, Germany — [2]DELTA - Technische Universität Dortmund, Maria-Goeppert-Mayer-Str. 2, D 44227 Dortmund, Germany

Self assembled monolayers (SAMs) of organic molecules on metal surfaces are of great interest for the development of nanoscale mechanic and electric devices. The adsorption of alkanethiolate SAMs on Au(111) has been extensively investigated in a large number of studies. Another system with increasing research activities in the last years are C_{60} fullerenes which have potential applications in several fields of nanotechnology. In this work the assembly of C_{60} buckyballs on a thiolated Au(111) surface was studied with in situ STM investigations. This allows new arrangements of physisorbed buckyballs on metal surfaces. CH_3S on gold was prepared exposuring a clean Au(111) surface to different partial preassures of Dimethyldisulfid (DMDS) yielding SAMs with different surface orientations. On these monolayers C_{60} buckyballs were evaporated. Instead of the standard close packed hexagonal arrays the C_{60} buckyball monolayers form striped phases depending on the underlying CH_3S phases.

O 14.10 Mon 17:15 H36

Building 2D crystals from fivefold-symmetric molecules — •Tobias Bauert[1], Leo Merz[1], Manfred Parschau[1], Jay S. Siegel[2], Georg Koller[3], and Karl-Heinz Ernst[1,2] — [1]Empa, Nanoscale Material Science, Dübendorf, Switzerland — [2]Organisch-chemisches Institut, Universität Zürich, Switzerland — [3]Institut für Physik, Karl-Franzens-Universität, Graz, Austria

Curved surface fragments of the fullerene molecule, so-called buckybowls, are promising candidates for surface modifications because of their unique electronic and chemical properties. Corannulene ($C_{20}H_{10}$) is the simplest curved fullerene fragment with a central C_5 ring, surrounded by five aromatic C_6 rings. Due to this fivefold symmetry, it is also a fascinating molecule for studies of fundamental phenomena in adsorbed monolayers, like molecular and chiral recognition or spontaneous symmetry breaking. Fivefold symmetry is incompatible with the translational order of a classical crystal lattice, which applies to plane group symmetries of 2D crystals grown at surfaces as well. Corannulene forms a quasi-hexagonal lattice by tilting away from the C_5 symmetry. Bulky substituents, however, do not allow a tilt and enforce C_5 as tiling motif. The observed molecular structures in STM are compatible with mechanical modeling experiments and Monte-Carlo simulations of hard pentagons. Apart from the self-assembly results, adsorbed corannulene shows interesting electronic properties, like induction of a large interface dipole moment (9 D), as determined with workfunction change measurements via UPS.

O 14.11 Mon 17:30 H36

2D-grids as precursors for 2D-crystals — •Thomas Waldmann, Christina Nenon, Robert Reichert, Harry E. Hoster, and R. Jürgen Behm — Institute of Surface Chemistry and Catalysis, Ulm University, D-89069 Ulm, Germany

The bis(terpyridine) derivative 2,4'-BTP [1,2] forms ordered monolayers (ML) on Ag(111)/Ru(0001) [3-5], Au(111) [3,5], highly ordered pyrolytic graphite (HOPG) [1-3,5], and Ag(100) at coverages between 0.35 and 0.44 molecules/nm^2. At T = 300 K and lower coverage, the adsorbates form a two-dimensional (2D) admolecule gas, where they move faster than the STM-tip. At T = 115 K, one can observe (2,4'-BTP)$_n$ oligomer chains stabilized by C-H···N-type hydrogen bonds. We show that the local configurations of the molecules and their individual orientations with respect to the substrate are similar to those known from ordered structures formed by the molecules at higher coverages. This confirms our previous suggestion that the corrugation of the molecule-substrate potential and the molecule-molecule interactions play an equally important role for the structures formed by this kind of molecules [3-4].

[1] U. Ziener et al., *Chem.Eur.J.* 8, **2002**, 951.
[2] C. Meier et al., *J.Phys.Chem.B* 109, **2005**, 21015.
[3] H.E. Hoster et al., *Langmuir* 23, **2007**, 11570.
[4] M. Roos et al., *Phys.Chem.Chem.Phys.* 9, **2007**, 5672.
[5] M. Roos et al., *Phys.Chem.Chem.Phys.*, DOI: 10.1039/b920481d