

O 52: Organic/bio Molecules on Metal Surfaces V

Time: Wednesday 16:00–19:00

Location: H38

O 52.1 Wed 16:00 H38

Steering on-surface self-assembly of high-quality hydrocarbon networks with terminal alkynes — ●NENAD KEPEČIJA¹, YI-QI ZHANG¹, MARTIN KLEINSCHRODT¹, JONAS BJÖRK², SVETLANA KLYATSKAYA³, FLORIAN KLAPPENBERGER¹, MARIO RUBEN^{3,4}, and JOHANNES V. BARTH¹ — ¹Physik Department E20, Technische Universität München, James-Franck-Straße, 85748 Garching, Germany — ²Department of Physics, Chemistry and Biology (IFM), Linköping University, 58183 Linköping, Sweden — ³Institute of Nanotechnology, Karlsruhe Institute of Technology, 76344 Eggenstein-Leopoldshafen — ⁴IPCMS-CNRS, Université de Strasbourg, 23 Rue de Loess, 67034 Strasbourg, France

The 2D self-assembly of 1,3,5-triethynyl-benzene (TEB) and *de novo* synthesized 1,3,5-tris-(4-ethynylphenyl)benzene (Ext-TEB) on Ag(111) was studied by means of scanning tunneling microscopy (STM) under ultra-high vacuum (UHV) conditions. Both molecules form nanoporous networks exhibiting organizational chirality, mediated by novel, planar six-fold cyclic binding motifs. Comparison with bulk structures of similar molecules suggests that these motifs appear only in 2D environments. The key interaction is identified as C–H... π bonding. For Ext-TEB an additional open-porous phase exists. The nature of the underlying non-covalent bonding schemes is analyzed by the density functional theory (DFT) calculations. Comparison of the calculations focusing on isolated 2D molecular sheets and those including the substrate reveals the delicate balance between molecule-molecule and molecule-substrate interactions.

O 52.2 Wed 16:15 H38

Differences in Chiral Expression: Racemic and Enantiopure Heptahelicenes on Various Metal Surfaces — ●JOHANNES SEIBEL¹ and KARL-HEINZ ERNST^{1,2} — ¹Empa, Nanoscale Materials Science, Dübendorf, Switzerland, Dübendorf, Switzerland — ²University of Zürich, Zürich, Switzerland

Previous scanning tunneling microscopy (STM) studies^[1,2,3] of racemic and enantiopure heptahelicenes (rac-[7H], M-[7H] or P-[7H]) on Cu(111) showed the formation of mirror domains. However, these domains consist of both enantiomers in an equal ratio and naturally, pure M- and P-[7H] form different structures. To investigate the influence of the metal surface on the two-dimensional ordering of heptahelicenes, we deposited rac-[7H] and M-[7H] on Cu(100), Ag(111) and Au(111). STM measurements reveal different expressions of chirality. On Ag(111) and Au(111) rac-[7H] forms a double-row structure similar to Cu(111), but no enantiomorphous domains are observed. Additionally, the structures of M-[7H] are very similar to the ones observed on Cu(111). In contrast to the structures on the 111-terminated surfaces containing both heptahelicene enantiomers, rac-[7H] on Cu(100) separates into enantiomorphous domains containing only M-[7H] or P-[7H], respectively.

[1] R. Fasel, M. Parschau and K.-H. Ernst, *Nature* 2006, 439, 449-452 [2] R. Fasel, M. Parschau and K.-H. Ernst, *Angew. Chem. Int. Ed.* 2003, 42, 5178-5181 [3] M. Parschau, R. Fasel and K.-H. Ernst, *Cryst. Growth & Des.* 2008, 8, 1890-1896

O 52.3 Wed 16:30 H38

Stereochemistry of C₄ dicarboxylic acids on Cu(110) — ●CHRYSANTHI KARAGEORGAKI¹ and KARL-HEINZ ERNST^{1,2} — ¹EMPA, Nanoscale Materials Science, Dübendorf, Switzerland — ²Chemistry department, University of Zürich, Zürich, Switzerland

In order to better understand self assembly at the molecular level, we are studying different chiral butanedioic acids, like tartaric acid (TA), malic acid (MA) and 2,3-dimethyl succinic acid (DMSU), as well as achiral analogues like succinic acid (SU), maleic acid (MEA), fumaric acid (FUA), meso-DMSU and trans 1,2-cyclohexane dicarboxylic acid (CHDCA) on Cu(110). Here we present LEED, STM and TPD results of the aforementioned compounds. Apart from coverage dependent "surface explosion" decomposition, all achiral compounds undergo chiral symmetry breaking, observed as superposition of mirror domains in LEED. Interestingly, the obtained LEED structures coincide for the various compounds, suggesting that the chiral recognition at surfaces derives from the substrate, in particular, when the molecule doesn't have functional groups to form strong intermolecular bonds. STM reveals that the substrate is "etched", leading to chiral reconstructions

of the surface.

O 52.4 Wed 16:45 H38

Orientation- and site-dependent electronic structure of a molecule on Au(111) investigated by STM and DFT with dispersion corrections — ●MAYA LUKAS¹, KARIN FINK¹, KER-RIN DÖSSEL¹, ALEXANDRINA SCHRAMM¹, CHRISTOPHE STROH¹, OLAF FUHR¹, MARCEL MAYOR^{1,2}, and HILBERT VON LÖHNESEN^{1,3} — ¹Karlsruher Institut für Technologie (KIT), Institut für Nanotechnologie, D-76021 Karlsruhe — ²Universität Basel, Department of Chemistry, CH-4056 Basel — ³Karlsruher Institut für Technologie (KIT), Physikalisches Institut und Institut für Festkörperphysik, D-76021 Karlsruhe

The exact orientation and bonding of a molecular wire to the connecting electrodes has a crucial effect on the conductance. Determining the exact bonding configuration as well as the electronic properties in the same experiment is hardly ever achieved, if possible at all.

We investigated a molecule that consists of three identical molecular wires connected in a rigid conformation. Due to the molecules chiral form the wires become different when coupled to a Au(111) surface. By scanning tunneling microscopy and density functional theory with dispersion corrections we study the local electronic structure of the molecular wires. We find strong variations of the electronic structure for wires with different orientation with respect to the surface within one molecule. Furthermore, the effect a positional shift of the whole molecule on the surface is investigated. From our calculations we are able to distinguish effects due to structural rearrangements in the molecule from effects due to electronic interaction with the surface.

O 52.5 Wed 17:00 H38

From achiral molecules to chiral superstructures: triphenylamine derivatives on Au(111) — ●KATHRIN MÜLLER¹, STEFANO GOTTARDI¹, JUAN CARLOS MORENO-LOPÉZ², KLAUS MÜLLEN³, MILAN KIVALA⁴, and MEIKE STÖHR¹ — ¹Zernike Institute for Advanced Materials, University of Groningen, Netherlands — ²Centro Atómico Bariloche-Instituto, Balseiro-CNEA-UNCuyo-CONICET, Río Negro, Argentina — ³Max Planck Institute for Polymer Research, Mainz, Germany — ⁴Department of Chemistry and Pharmacy, University of Erlangen-Nürnberg, Germany

We investigated the self-assembly of achiral triphenylamine derivatives, so-called heterotriangulenes, which feature cyano functionalities intended for intermolecular dipolar coupling, on Au(111). We observed the coexistence of two phases, both expressing chirality. Deposition of one monolayer leads to the formation of a hexagonally closed packed phase. For submonolayer coverage numerous vacancies are present, which organize spontaneously forming a porous network. The second phase is stabilized by the introduction of metal-coordinated bonds and also exhibit pores. The structural models of the different binding motives of these two phases, the intermolecular interactions as well as the influence of the substrate on the assembly will be discussed. Moreover, we investigated the effect of post-annealing onto the assembly structure. We observed a partial transformation of one phase into the other. This spontaneous assembly of molecules into chiral and porous network structures on surfaces is of great interest for many future applications for example in catalysis, opto-electronics or as sensors.

O 52.6 Wed 17:15 H38

On-surface polymerization of biphenyl derivatives on Ag(111) — ●FEI SONG¹, TUAN ANH PHAM¹, SERPIL BOZ², UMUT SOYDANER³, MARCEL MAYOR³, and MEIKE STÖHR¹ — ¹Zernike Institute for Advanced Materials, University of Groningen, 9747AG, the Netherlands — ²Department of Physics, University of Basel, Switzerland — ³Department of Chemistry, University of Basel, Switzerland

The controlled assembly of molecular building blocks, which possess functional units for switching, subsequent covalent interlinking etc., into functional architectures on surfaces has become an established research fields over the past decades [1]. However, the structures which are based on non-covalent interactions mostly lack mechanical stability. In view of possible future applications higher stability and the prospect of improved charge transport are important requirements. In this work, a unique concept to control both the molecular self-assembly and the subsequent intermolecular coupling was utilized through equipping the

molecular building blocks with terminal protecting groups. Specifically, biphenyl derivatives with BOC protecting groups were deposited onto a Ag(111) surface. STM and XPS were used to explore both the self-assembly behaviors and the on-surface polymerization after annealing the sample at elevated temperatures. It turned out that the protecting groups can be split off by annealing [2] and the deprotected monomers interlink into polymeric structures. By tuning the design of the organic monomers, the reactivity as well as the size of polymeric structures can be controlled. Reference [1] J.A.A.W. Elemans, *Angew. Chem. Int. Ed.* 48 (2009) 7298 [2] S. Boz et al., *Angew. Chem. Int. Ed.* 48 (2009) 3179

O 52.7 Wed 17:30 H38

Self-assembly of a threefold symmetric CN-terminated molecular linker on Cu(111) and Ag(111) — ●PETER B. WEBER¹, YIQI ZHANG¹, FLORIAN KLAPPENBERGER¹, SVETLANA KLYATSKAYA², MARIO RUBEN^{2,3}, and JOHANNES BARTH¹ — ¹Physik Department E20, Technische Universität München, Garching 85748, Germany — ²Institute of Nanotechnology, Karlsruhe Institute of Technology — ³Institut de Physique et Chimie des Matériaux de Strasbourg, Université de Strasbourg

We present a scanning tunneling microscopy study of the self-assembly of 1,3,5-tri(4-cyanophenyl)-benzene (TCB) on the Cu(111)-surface and on the Ag(111)-surface. The measurements were carried out under ultra-high-vacuum conditions at 5.5 K. On both surfaces the formation of large regular networks was observed. The molecules are arranged in a hexagonal lattice and the islands are stabilized by multiple proton acceptor ring interactions [1]. This behavior contrasts that for linear NC-Ph_x-CN species where multiple nanoporous networks were formed partially involving dipolar interactions [2]. The formed networks are commensurable with the Cu(111)-surface but not with the Ag(111)-surface. In a second step we demonstrate the usefulness of these islands to steer the positioning of Co-atoms resulting in a high yield of Co-phenyl half-sandwich compounds with potentially interesting magnetic properties.

[1] Arras, E. et al, *Phys. Chem. Chem. Phys.* 14, 15995 (2012) [2] Kühne, D. et al, *J. Phys. Chem. C* 113, 17851 (2009)

O 52.8 Wed 17:45 H38

The metal | ionic liquid interface: Adsorption behavior of ionic liquid adlayers on Cu(111) — STEPHAN GABLER^{1,2}, ●BENEDIKT UHL^{1,2}, FLORIAN BUCHNER^{1,2}, and R. JÜRGEN BEHM¹ — ¹Ulm University, Institute of Surface Chemistry and Catalysis, D-89069 Ulm, Germany — ²Helmholtz-Institute Ulm (HIU) Electrochemical Energy Storage, D-89069 Ulm, Germany

Ionic liquids (IL's) are promising electrolytes in Li-Ion batteries. The behavior of IL's at the electrode | electrolyte interface is crucial for the performance of such electrochemical systems, studies on this topic, however, are at their very beginning. In this work, we investigated the adsorption behavior of 1-Butyl-1-methylpyrrolidinium-bis(trifluoromethylsulfonyl)imide (BMP TFSA) on Cu(111) in the submonolayer and monolayer range. Combined STM and XPS investigations were conducted under UHV conditions and at temperatures between 100 K and 298 K. Compared to the XPS bulk signals, additional peaks are found in the N1s and S2p region for thin BMP-TFSA adlayers. The additional S2p peak indicates a sulfidic species on the surface (e.g. Cu₂S), which we assume is due to a partial decomposition of the anion. In STM, two different structures are observed on the surface: the first is stable at room temperature and the second is solely found below 170 K. Additionally the Cu-steps are altered, which indicates the participation of the metal surface in the decomposition reaction. Presumably, the first structure represents decomposition products and the second one intact IL molecules.

O 52.9 Wed 18:00 H38

The metal | ionic liquid interface: Comparison of the adsorption behavior of different ionic liquids on Ag(111) — ●FLORIAN BUCHNER^{1,2}, BENEDIKT UHL^{1,2}, DOROTHEA ALWAST^{1,2}, HSINHUI HUANG^{1,2}, and ROLF-JÜRGEN BEHM^{1,2} — ¹Helmholtz-Institute Ulm (HIU) Electrochemical Energy Storage, D-89069 Ulm, Germany — ²Ulm University, Institute of Surface Chemistry and Catalysis, D-89069 Ulm, Germany

Ionic liquids are promising candidates as electrolytes in Li-ion batteries, which play a key role in energy storage devices. In this model approach, we aim towards a molecular understanding of the processes at the metal electrode | ionic liquid interface. 1-butyl-1-methylpyrrolidinium-bis(trifluoromethylsulfo-

nyl)imide [BMP]⁺[TFSA]⁻ and 1-ethyl-3-methylimidazolium-bis(trifluoromethylsulfonyl)imide [EMIM]⁺[TFSA]⁻ on Ag(111) are studied at mono- and submonolayer coverages by scanning tunneling microscopy (STM) under UHV conditions in the temperature range between 100 K and room temperature. [BMP]⁺[TFSA]⁻ exists in a highly mobile 2D gas phase in the range between 300 K and 100 K, i.e., it exhibits a low diffusion barrier. Additionally, at 100 K a long-range ordered and homogeneous 2D solid phase fills up large terraces, and a 2D disordered phase is found close to steps. Dynamic STM measurements highlight exchange of adspecies at the phase boundary between 2D solid and 2D gas phase. The adsorption behavior of [BMP]⁺[TFSA]⁻ and [EMIM]⁺[TFSA]⁻ on Ag(111) is discussed, focusing on ordering aspects, diffusion properties and 2D melting.

O 52.10 Wed 18:15 H38

An explicit solvation model for the force field description of bis(terpyridine) adsorption — ●DANIELA KÜNZEL and AXEL GROSS — Institute for Theoretical Chemistry, Ulm University, D-89069 Ulm, Germany

In the theoretical modeling of organic adlayers that are deposited from solution the solvent is typically not taken into account.[1] Instead, calculations are often carried out at the solid/vacuum interface. DFT and force field simulations of bis(terpyridine) (BTP) adsorption have shown that even such a simple model is able to reproduce and explain experimental observations made at the solid/liquid interface.[2] However, any effects the solvent might have on the system remain unknown.

Thus we now present the use of an explicit solvation model for the force field simulation of the ordered BTP adsorption on graphite. Even though different force fields yield different quantitative values for the energetics of the molecules in solution, the effect of solvation can at least be distinguished in a qualitative way.

The calculations show that solvation has a significant effect on the thermochemistry of BTP adsorption. Properties of the ordered adsorbate layers are also affected by these changes. Finally, taking solvation into account can also help to gain a deeper understanding of the structure formation process.

[1] Kucera, J.; Groß, A. *Langmuir* 2008, 24, 13985.

[2] Meier et al. *J. Phys. Chem. C* 2010, 114, 1268-1277. Künzel et al. *Phys. Chem. Chem. Phys.* 2009, 11, 8867-8878.

O 52.11 Wed 18:30 H38

The role of dispersion forces in SAM(aromatic thiolates)/Au(111) systems: a DFT study including semiempirical dispersion corrections — ●JAN KUČERA and AXEL GROSS — Institut für Theoretische Chemie, Universität Ulm, D-89069 Ulm, Germany

The anchoring of aromatic thiolates on metal substrates has been widely used as a feasible method to effectively modify the electronic properties of environment/metal interfaces intended as, e.g., components of new nanoelectronic devices. The theoretical description of those systems represents a rather complex task since also noncovalent effects as, e.g., van der Waals (vdW) interactions operate in the formation of the complexes.

We performed periodic density functional theory (DFT) calculations with semiempirical DFT-D3 [1] and DFT+vdW [2] corrections to clarify the role of dispersion in the molecule-surface as well as in the molecule-molecule interaction. To be specific, we addressed SAM/Au(111) complexes with the SAM formed by di-4-pyridine-di-sulphide (PySSPy), 4-mercaptopyridine (SPy), and 4-(4-mercaptophenyl) pyridine (SPhPy) molecules. We find that the stability of the PySSPy/Au complex is dominated by dispersion. In contrast, covalent bonding is the structure- and stability-determining factor in SPy and SPhPy/Au complexes, where dispersion only significantly contributes to the molecule-substrate interaction.

[1] S. Grimme et al., *J. Chem. Phys.* 132, 154104 (2010).

[2] A. Tkatchenko and M. Scheffler, *PRL* 102, 073005 (2009).

O 52.12 Wed 18:45 H38

DFT Studies on the Adsorption of Atomic Sulfur and Methanethiolate at the Cu(111) Surface — ●PORNTIP SEEMA, JÖRG BEHLER, and DOMINIK MARX — Lehrstuhl für Theoretische Chemie, Ruhr-Universität Bochum, D-44780 Bochum

Density-functional theory (DFT) calculations have been employed to study the adsorption of atomic sulfur and methanethiolate at the Cu(111) surface. A large number of surface models has been investigated considering a variety of adsorbate phases, binding sites and

surface coverages. The results show that the adsorption of atomic sulfur and methanethiolate gives rise to surface reconstructions. The most preferable phase for atomic sulfur contains three sulfur atoms in the unit cell and three copper atoms in the reconstructed layer. For methanethiolate, several similar local minima exist differing in the

positions of copper atoms in the reconstructed layer and these calculated structures deviate from the perfect fourfold Cu-S coordination observed in STM. Furthermore, modifying the chemical composition of the relaxed layer, e.g. by adding another copper atom, yields structures of comparable stability.