

O 59.6 Thu 10:45 MA 041

Aromatic vs. Hydrogen Bonds in Self-Assembled Monolayers of Organic Molecules, a STM-Study — ●RICO GUTZLER, SOPHIE LAPPE, WOLFGANG M. HECKL, and MARKUS LACKINGER — LMU München, Sektion Kristallographie, Theresienstr. 41, 80333 München

The monolayer structure of two distinct organic molecules is investigated by STM. We demonstrate how a small modification of a polycyclic aromatic molecule, which does not affect the functional groups, can have dramatic impact on the structure of the self-assembled monolayer. Both molecules exhibit C₃ symmetry, have a central benzene ring in common and three carboxylic groups at the 1,3,5 positions, each separated by a rigid spacer. One compound exhibits methyl groups at the 2,4,6 positions of the central benzene ring, the other remains unsubstituted. This change in molecular structure was found to result in completely different self-assembly behaviour at the liquid-graphite interface. The unsubstituted molecule adsorbs in a row structure, where the molecules are stacked with their planes almost perpendicular to the substrate. The methylated molecule self-assembles into a sixfold chickenwire network where the molecules are adsorbed planar. Based on our experimental finding and supported by force field calculations, we propose that in the first case the intermolecular binding is dominated by aromatic interaction between the extended pi-electron systems, whereas in the latter case the chickenwire structure is driven by twofold intermolecular hydrogen bonds between the peripheral carboxylic groups. This finding is explained by weakening of the pi-pi stacking due to steric hindrance imposed by the methyl groups.

O 59.7 Thu 11:00 MA 041

Template Readout of Hierarchical Coordination Networks at Surfaces — ●ALEXANDER LANGNER¹, STEVEN L. TAIT¹, NIAN LIN¹, CHANDRASEKAR RAJADURAI², MARIO RUBEN², and KLAUS KERN^{1,3} — ¹Max-Planck-Institut für Festkörperforschung, Stuttgart — ²Forschungszentrum Karlsruhe GmbH — ³Ecole Polytechnique Fédérale de Lausanne, Switzerland

Self-assembly of organic molecules into supramolecular networks is an efficient strategy to pattern surfaces with functional nanostructures. Highly ordered architectures can be achieved if the spontaneous self-organization process is steered by selective and directional non-covalent interactions. Here we demonstrate that from a mixture of organic ligands, several unique structures can be "read out" by adjusting the external environment of the mixture. We report on the self-organization of mixtures of multiple ligands with metal atoms at the Cu(100) surface under ultra high vacuum (UHV) conditions. The generated architectures exhibit a hierarchy of supramolecular interactions: highly stable metal-organic coordination bonding and somewhat weaker hydrogen bonding. With scanning tunneling microscopy (STM) we demonstrate that modification of external parameters, e.g. commensurability with substrate or introduction of guest molecules, causes distinct structural configurations for identical ligand binding units, even leading in some cases to complete ligand segregation. Due to the hierarchy of bonding strengths, it is possible to modify only the lower level of structural organization resulting in new metal-organic architectures with identical primary structural units.

O 59.8 Thu 11:15 MA 041

Structure and Charge Transfer in Metal-TCNQ Complexes on Cu (100) — ●TZU-CHUN TSENG¹, STEVEN L. TAIT¹, XIONG LIU¹, NIAN LIN¹, and KLAUS KERN^{1,2} — ¹Max Planck Institute for Solid State Research, Heisenbergstraße 1, 70569 Stuttgart, Germany — ²Institut de Physique des Nanostructures, Ecole Polytechnique Fédérale de Lausanne (EPFL), 1015 Lausanne, Switzerland

Organic-based alternatives to conventional magnets offer the possibility to form self-organized nanometer-scale structures at surfaces with specific magnetic properties. For example, coordination compounds of metal ions (M) with the organic molecule 7,7,8,8-

tetracyanoquinodimethane (TCNQ) in solution have been shown recently to have a high magnetic ordering temperature for large M:TCNQ ratios (R. Jain et al., Nature 445 (2007) 291-294). A critical issue for the development of metal-organic structures in magnetic or electronic applications is the relationship of electronic configuration to physical structure. Here we correlate structural information of 2D M-TCNQ (M = Mn, Fe, Co, Ni, Cu) networks from scanning tunneling microscopy and low energy electron diffraction with charge transfer information obtained by X-ray photoemission spectroscopy. M-TCNQ mixtures at Cu(100) self-organize into ordered structures, whose coordination ratio and domain size depend strongly on the choice of metal. XPS results identify distinct core level shifts in N 1s spectra of M-TCNQ for 2D coordination to different metal centers compared to neutral TCNQ.

O 59.9 Thu 11:30 MA 041

Video-STM investigation of the dynamic behavior of bis-terpyridine submonolayers on Ag(111)-oriented films — ●THOMAS WALDMANN, HARRY E. HOSTER, and R. JÜRGEN BEHM — Institute of Surface Chemistry and Catalysis, Ulm University, D-89069 Ulm, Germany

We present a quantitative analysis of the dynamic exchange of single molecules between two phases [1] of a bis-terpyridine derivative (2,4'-BTP) [2] adlayer adsorbed on Ag(111)-oriented thin films on Ru(0001). The analysis is based on video-STM measurements in ultra high vacuum at room temperature. The adlayer was produced by evaporation on a highly ordered (111)-oriented Ag film, which leads to the formation of a quasi-quadratic network (QQN) [2, 3]. Via thermal desorption it is possible to create defects in the QQN, which leads to a new disordered phase with a quasi-hexagonal short-range order (QHP). Depending on the BTP coverage 70-90% of the molecules in the QHP are rotating, while the rest exhibits preferred orientations in steps of 30°. At the QQN/QHP phase boundary, we observed molecules jumping back and forth between both phases. From the different probabilities to find the molecules in either phase we estimated the corresponding energy difference via a Boltzmann-approach.

[1] Poster O 18.58

[2] C.Meier et al., J.Phys.Chem.B 109, 21015 (2005)

[3] H.E.Hoster et al., Langmuir 23, 11570 (2007)

O 59.10 Thu 11:45 MA 041

Bottom-up construction of covalently bound molecular nanostructures — ●LEONHARD GRILL¹, MATTHEW DYER², LEIF LAFFERENTZ¹, MATS PERSSON², MAIKE PETERS³, and STEFAN HECHT³ — ¹Institut für Experimentalphysik, Freie Universität Berlin, Arnimallee 14, Berlin — ²Department of Chemistry, University of Liverpool, Liverpool L69 3BX, UK — ³Institut für Chemie, Humboldt-Universität zu Berlin, Brook-Taylor-Str. 2, Berlin

The ultimate goal of molecular electronics consists in the use of single functionalized molecules for circuits at the atomic scale. In possible future applications, such molecular arrays need to be highly stable and allow charge transport between the molecular building blocks. Hence, covalent bonds are desired for the intermolecular connections. However, up to now only rather weak interactions have been reported for supramolecular networks on surfaces.

We report on the controlled formation of covalently bound networks of porphyrin molecules on a gold surface upon deposition of thermally activated molecular building blocks and their subsequent chemical reaction at predefined connection points [1]. Scanning tunneling spectroscopy measurements, lateral manipulation, and density functional theory calculations unambiguously reveal the covalent character of the intermolecular bonds. Furthermore, we show that the dimensions and shape of these nanostructures can be precisely engineered by controlling the number of bromine substituents of the molecular building block, leading to the formation of dimers, chains and networks.

[1] L. Grill et al., Nature Nanotech. 2, 687 (2007).