

Thursday Afternoon, November 12, 2009

Surface Science

Room: N - Session SS2-ThA

Supramolecular Interfaces by Design

Moderator: Y. Chabal, University of Texas, Dallas

2:00pm **SS2-ThA1 Cyano-directed Self-assembly of n-modular Porphyrin Oligomers at Surfaces: The Delicate Balance Between Competing Interactions**, *N.P. Reynolds*, The University of Basel, Switzerland, *L.-A. Fendt*, ETH Zurich, Switzerland, *M. Stöhr*, *N. Wintjes*, *M. Enache*, The University of Basel, Switzerland, *T.A. Jung*, Paul Scherrer Institute, Switzerland, *F. Diederich*, ETH Zurich, Switzerland

The self-assembly properties of two cyano (CN) functionalized porphyrin isomers on Cu(111) were studied at different coverages by means of scanning tunneling microscopy (STM). Both isomers have two voluminous 3,5-bis(*tert*-butyl)phenyl substituents and two rod-like 4-cyanobiphenyl substituents in *cis* and *trans* configurations. For coverages up to one monolayer, the *cis* porphyrins were found to form a variety of oligomeric clusters ranging from dimers to hexamers, held together by cyanophenyl directed anti-parallel dipole-dipole interactions, hydrogen bonding and metal complexation. Furthermore, small changes in preparation conditions were also found to have a profound effect on the size distribution of the clusters. This variety and size distribution of the oligomers demonstrates how the delicate balance between the strength of adsorbate-adsorbate and adsorbate-substrate interactions has a major effect on self-assembly.

Previous work from Yokoyama *et al.*, using a similar molecule with shorter cyanophenyl binding groups formed exclusively tetrameric structures on less reactive Au(111) substrates. In this study high resolution STM images showed the presence of structures ranging from dimeric to hexameric, as well as chainlike structures. On the basis of this data we conclude that on the more reactive Cu(111), the very strong adsorbate-substrate interactions present are the dominating influence, leading to the multimorphism of binding motifs and oligomers observed.

[1] T. Yokoyama, S. Yokoyama, T. Kamikado, Y. Okuno, S. Mashiko, *Nature* **2001**, *413*, 619-621.

2:20pm **SS2-ThA2 The Directed Assembly of TiOPc - C₆₀ Films: Three Structural Motifs**, *Y. Wei*, University of Maryland, *S. Robey*, National Institute of Standards and Technology, *J. Reutt-Robey*, University of Maryland

A key strategy for the improvement of organic electronic devices involves the optimization of chemical morphology on the interfaces of donor-acceptor heterojunctions for efficient charge separation. Fundamental studies of chemical morphology - electronic property relations, particularly along crucial domain boundaries, are needed to realize these goals. We present STM/STS studies of TiOPc: C₆₀ films, prepared in three dramatically different structural motifs: (1) Nanophase segregated TiOPc and C₆₀ domains, (2) A co-crystalline TiOPc₍₂₎C₆₀₍₁₎ honeycomb network and (3) A regular array of triangular TiOPc domains and C₆₀ nanoclusters with a 10 nm repeat. Motif selection is accomplished through anisotropic TiOPc-TiOPc interactions, under the process control of TiOPc deposition rates. Subsequent C₆₀ deposition on these pre-engineered TiOPc films yields these three distinct structural motifs. Chemical morphology-electronic relations are then determined via Z (V) STS spectroscopy. Electronic transport gaps vary weakly (~0.2 eV) by C₆₀-TiOPc phase. Significantly, an ~0.5 eV increase in the transport gap appears along heterointerface boundaries. We present structural models for each hetero interface and discuss the physical origin of the observed transport characteristics.

This work has been supported by the National Science Foundation under Surface Analytical Chemistry grant CHE0750203 and the Dept. of Commerce through the NIST small grants program.

2:40pm **SS2-ThA3 Supramolecular Engineering in Two Dimensions**, *J.V. Barth*, Technische Universität München, Germany **INVITED**

The application of biologically inspired organization principles to artificial environments opens up intriguing vistas for the design of complex interfaces. Here we focus on well-defined metal surfaces serving as platforms to handle molecular building blocks with specific functionalities. We employ scanning tunneling microscopy for molecular-level imaging of both single molecules and self-assembled systems, whereas scanning

tunneling spectroscopy captures the pertaining electronic properties. Distinct nanoarchitectures, such as biomolecular gratings, metal-organic arrays and porous nanomeshes, are realized through molecular recognition and selective hydrogen bonds, zwitterionic or metal-ligand interactions. Complementary insight from space-averaging techniques and computational modeling allows for the comprehensive assessment of structure-functionality correlation, notably including quantum confinement, chemical reactivity and magnetism. It is suggested that this supramolecular engineering strategy provides a versatile rationale to design unique nanosystems. Their tunable structural and functional characteristics bear promise for future technological applications.

3:40pm **SS2-ThA6 Functionalized C₆₀ SAMs Diversity Via Molecular Conformation Variability**, *B. Diaconescu*, University of New Hampshire, *T. Yang*, Michigan State University, *M. Jazdzzyk*, *G. Miller*, University of New Hampshire, *D. Tomanek*, Michigan State University, *K. Pohl*, University of New Hampshire

Self-assembled organic thin films have a great number of practical applications, ranging from sensors and biological interfaces in medical implants to organic electronics and photovoltaics. Self-assembled monolayers (SAMs) form as a result of a delicate balance between competing molecule-substrate and intermolecular interactions. In order to control such self-organization processes, it is crucial to understand how this balance reflects onto the SAM's equilibrium structure. We will present a STM/DFT study of the self-assembly of C₆₀ functionalized with alkyl chains of various lengths (F-C₆₀) on Ag(111). We find that various structures are forming as a function of the alkyl chain lengths, ranging from zigzag to linear arrays of C₆₀ cages, and they are driven by molecular conformational changes induced by the interaction with the surface. The symmetry of the F-C₆₀ SAM is dictated by the molecular conformation, a consequence of molecule-surface interaction, while the size of the unit cell is a consequence of the intermolecular interactions. These results show that C₆₀s can be assembled in 2D and non-compact molecular arrays with a unit cell symmetry and size controllable via appropriate chemical functionalization.

4:00pm **SS2-ThA7 Electronic Confinement Imposed by a Nanoporous Supramolecular Network**, *M. Matena*, *J. Lobo-Checa*, *M. Wahl*, University of Basel, Switzerland, *H. Dil*, University of Zürich, Switzerland, *L.H. Gade*, University of Heidelberg, Germany, *T.A. Jung*, Paul Scherrer Institute, Switzerland, *J. Zegenhagen*, ESRF, France, *M. Stöhr*, University of Basel, Switzerland

Molecular assemblies on surfaces can be used as templates that allow the study of host guest interactions and provide in a further step an ideal starting point for the generation of more complex hierarchic structures. An important prerequisite besides the regularity of such structures is their stability.

We reported the formation of a molecular honeycomb network generated by thermal dehydrogenation of a perylene derivative (DPDI) on a Cu(111) surface [1]. By thermal activation, these molecules become H-bond donors/acceptors and form a highly regular honeycomb structure which is commensurate to the Cu substrate. This network can be used as a template for the incorporation of guest molecules in its hexagonal "holes" [2], [3]. Besides utilizing this network for the study of guest molecules, XSW (x-ray standing wave) experiments were carried out to gain more structural information and by this more information on the molecule substrate interaction. This is done by determining the vertical height of the molecules above the Cu surface before and after annealing the sample. Before annealing, the DPDI molecule is chemisorbed. It mainly interacts via its N atoms with the Cu surface and is in a bridge-like configuration. After annealing, the height difference between the end groups and the perylene core is lowered what is required to enable H-bonding between the molecules.

Furthermore, to study the interaction between the electronic Cu surface state and the DPDI network, scanning tunneling spectroscopy (STS) and angle-resolved photoemission spectroscopy (ARPES) were used. Each pore of our porous network confines the Cu surface state in what can be described as a 0D quantum dot. Due to the imperfect confinement observed for all 0D cases studied so far on surfaces, the quantum dots couple with their neighbors resulting in shallow dispersive electronic bands [4]. A consequence of this work is the perspective to engineer these artificially created electronic structures by modification of the dimensions of the molecular network periodicities together with the appropriate choice of the substrate.

[1] M. Stöhr et al., *Angew. Chem. Int. Ed.* 44 (2005) 7394; [2] M. Wahl et al., *Chem. Commun.* (2007) 1349; [3] M. Stöhr et al., *Small* 3 (2007) 1336; [4] J. Lobo-Checa et al., submitted.

4:20pm **SS2-ThA8 Surface Supported Chain Formation of Magnetic Molecules**, *S. Chang*, University of Hamburg, Germany, *K. Clark*, *A. Dilullo*, Ohio University, *S. Kuck*, University of Hamburg, Germany, *S.-W. Hla*, Ohio University, *G. Hoffmann*, *R. Wiesendanger*, University of Hamburg, Germany

The last years showed a tremendous development into accessing and understanding the physics of metal-organic complexes in contact to a surface on a single molecule level. Molecular classes in the focus are often specialized but commercially available systems. Further progress towards device development requires molecular classes with a more flexible structure for functionalization.

In our contribution we introduce such a promising candidate, the so called Salens, and present first results on the local investigation by Scanning Tunneling Microscopy (STM). Salens are volatile metal-organic complexes with the metallic ion caged from three sides. Salens are chemically easily modified to tune the interaction with a substrate, with neighboring molecules, or to establish an intramolecular electronic and magnetic communication between two metallic centers through the organic periphery. Based on the paramagnetic Co-Salen, which shows no self-assembly on metallic substrates, we demonstrate that the exchange of a single atom in the molecular structure the interaction can be tuned from repulsive to attractive interaction[1]. Even surface-supported covalent bonding can be initiated to form larger entities. By means of STM, STS, and STM induced manipulation we will discuss the adsorption and the electronic properties of the parent Co-Salen and modified Salens on metallic and isolating surfaces.

Acknowledgements: This work was supported by the DFG within the GrK 611 and the SFB 668-A5, by the EU in the project "SPiDMe", and the NSF-PIRE program.

[1] S. Kuck et al., "Steering two dimensional molecular growth via dipolar interaction", accepted for publication in *ChemPhysChem* (2009).

4:40pm **SS2-ThA9 Reactive Adsorption to Ordered Bis-Terpyridine Networks**, *T. Waldmann*, *H.E. Hoster*, Institute of Surface Chemistry and Catalysis, Germany, *D. Künzel*, Institute of Theoretical Chemistry, Germany, *M. Roos*, *A. Breitruck*, Institute of Surface Chemistry and Catalysis, Germany, *A. Groß*, Institute of Theoretical Chemistry, Germany, *R.J. Behm*, Institute of Surface Chemistry and Catalysis, Germany

Using time resolved scanning tunneling microscopy, we tested the effect of O₂ exposure on ordered supra-molecular networks of Bis-terpyridine derivative molecules (2,4'-BTP)[1,2] supported on Au(111)[3], Ag(111)[3,4] and Graphite[3] (HOPG) substrates at T = 300 K. Under certain circumstances, our image sequences unambiguously show modifications of individual 2,4'-BTP molecules upon O₂ exposure and concomitant rearrangements within the hydrogen bonded adlayer. Furthermore, comparison of the behaviour on different substrates clearly shows that these modifications require a catalytically active surface.

The experimental observations are complemented by density functional theory calculations. In combination, both give rise to a probable model for the observed surface reactions and their effect on the supramolecular structure.

[1] U.Ziener et al., *Chem.Eur.J.* 8, 951, 2002

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

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

[4] M.Roos et al., *Phys. Chem. Chem. Phys.* 9, 5672, 2007

5:00pm **SS2-ThA10 Charge Transfer-Driven Molecular Self-Assembly at Organic/Metal Interfaces**, *T.-C. Tseng*, Max Planck Inst. for Solid State Res., Germany, *C. Urban*, *W. Yang*, Univ. Autonoma de Madrid, Spain, *R. Otero*, UAM & IMDEA-Nano, Spain, *S.L. Tait*, Max Plank Inst. for Solid State Res., Germany, *M. Alcami*, *D. Eciija*, *M. Trelka*, Univ. Autonoma de Madrid, Spain, *J.M. Gallego*, ICMM-CSIC, Spain, *M.A. Herranz*, Univ. Complutense de Madrid, Spain, *F. Martin*, Univ. Autonoma de Madrid, Spain, *N. Martin*, Univ. Complutense de Madrid, Spain, *K. Kern*, Max Plank Inst. for Solid State Res., Germany, *R. Miranda*, UAM & IMDEA-Nano, Spain

Organic heterostructures based on blends of molecules with electron-accepting (large electron-affinity) and electron-donating (small ionization potential) character display interesting electrical and optical properties with promising technological applications. For example, they show electroluminescence for Organic Light Emission Diodes (OLEDs),

photovoltaic response for solar cell devices and one-dimensional conduction for low molecular-weight metallic films, while strong acceptors or donors are the basis for metal-organic magnets. These blends of molecules are deposited onto or contacted with metallic layers and their performance depends crucially on the alignment of energy levels, the molecular nanostructure and crystalline perfection. Interfaces between organic species with either donor or acceptor character and metal surfaces are, thus, of paramount importance for the performance of the devices described above. This observation has motivated a large effort aimed at understanding the electronic structure of organic/metal interfaces and, in particular, the alignment of the energy levels at the interface related to the charge transfer between the organic donor or acceptor species and the metallic surface. Charge transfer, however, not only leads to modifications in the alignment of energy levels; usually, it is also related to structural transformations in both donating and accepting species. Unfortunately, too often it is assumed that the substrate is just an inert spectator, playing no active role in the supramolecular organization. We describe here experiments (STM, LEED, XPS) and theoretical simulations that unequivocally demonstrate that for strong charge transfer systems, such as the organic acceptor tetracyanoquinodimethane (TCNQ) deposited on Cu(100) both the molecules and the substrate suffer strong structural rearrangements that may even control the resulting molecular ordering. Such charge transfer-induced structural rearrangements at both sides of the organic/metal interface might have significant effects on the subsequent growth and structure of the organic film and, thereby, on device performance.

5:20pm **SS2-ThA11 Architectural Complexity, Intermolecular Interactions, and Charge Transfer in Supramolecular Networks at Surfaces**, *H. Adler*, *Y. Ge*, *S.L. Tait*, Indiana University

Self-assembly of two-dimensional supramolecular networks stabilized by hydrogen bonding or metal-organic coordination offers an efficient route to the rational design of functional surface architectures and provides a model system for (bio-)molecular assembly. These systems may contribute to advances in sensors, catalysis, molecular electronics, photovoltaics, and other thin film device applications. Such systems have been demonstrated to form highly-ordered, extended networks by selective and directional coordination bonding. Experiments were made using metal atoms and organic ligands containing carboxylic acid, cyano or pyridyl functional end groups, which were vapor deposited to atomically clean and flat surfaces. Structural characterization by scanning tunneling microscopy allows molecular level insight into the structure and assembly of the systems. X-ray photoelectron spectroscopy provides evidence for chemical interactions within the networks. High-resolution electron energy loss spectroscopy lends insight into intermolecular interactions. These experiments are correlated with density functional theory calculations for a better understanding of the bonding interactions that stabilize the highly ordered surface nanostructures. Binary mixtures of ligands allow for a large variety of metal-organic frameworks based on hierarchical assembly, co-crystallization, or cooperative multi-ligand coordination interactions. Current studies are focusing on understanding chemical function of these systems and how this can be tuned through supramolecular design strategies.

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