

## O 89: Metal substrates: Adsorption of organic / bio molecules V

Time: Friday 10:30–13:00

Location: A 053

O 89.1 Fri 10:30 A 053

**Self-assembly and 2D spontaneous resolution of cyano-functionalized [7] helicenes on Cu(111)** — •TUAN ANH PHAM<sup>1</sup>, SERPIL BOZ<sup>2</sup>, ANELIJA SHCHYRBA<sup>2</sup>, SYLWIA NOWAKOWSKA<sup>2</sup>, MICHAEL SCHÄR<sup>3</sup>, FRANÇOIS DIEDERICH<sup>3</sup>, MANH-THUONG NGUYEN<sup>4</sup>, DANIELE PASSERONE<sup>4</sup>, THOMAS JUNG<sup>5</sup>, and MEIKE STÖHR<sup>1</sup> — <sup>1</sup>University of Groningen, Netherlands — <sup>2</sup>University of Basel, Switzerland — <sup>3</sup>ETH Zürich, Switzerland — <sup>4</sup>EMPA, Switzerland — <sup>5</sup>PSI, Switzerland

Supramolecular control involves the selective recognition of chirality for any target assembly in order to shape e.g. the active elements within their environment. This refers equally to 3D crystal growth as well as to the field of surface-supported supramolecular assemblies. Notably, the spontaneous resolution of racemic compounds into separate enantiomeric crystals serves as an indicator for the enantioselective assembly governed by the specific intermolecular and - for surface supported assemblies - by molecule substrate interactions which can be considered as a complicating factor. Herein, we show the first example of a spontaneous chiral resolution of a helicene derivative on a Cu surface. Through STM and DFT investigations, the formation of fully segregated domains of pure enantiomers (2D conglomerate) from racemic dicyano[7]helicene were demonstrated. The propensity of the system to optimize intermolecular hydrogen bonding as well as dipolar interactions translates into chiral recognition. In addition, a discussion of the effect of chirality on the nucleation and formation of helicene chains for low coverage shall be presented.

O 89.2 Fri 10:45 A 053

**STM study of molecular structures of bis(phthalocyaninato)-lutetium(III) on crystalline substrates** — •LARS SMYKALLA, PAVEL SHUKRYNAU, and MICHAEL HIETSCHOLD — Chemnitz University of Technology, Institute of Physics, Solid Surfaces Analysis Group, D-09107 Chemnitz, Germany

Results of the adsorption and formation of self-assembled ordered molecular structures of the double-decker phthalocyanine molecule bis(phthalocyaninato)lutetium(III) on the anisotropic metallic surface of an Ag(110) single crystal and on highly oriented pyrolytic graphite (HOPG) are reported. We used a variable temperature scanning tunneling microscope (STM) at 30 K and room temperature under ultrahigh vacuum conditions to image the molecules with submolecular resolution. The electronic properties were investigated with scanning tunneling spectroscopy and density functional theory calculations for single molecules. The observed molecular structures and scanning tunneling spectroscopy results for both different substrates are compared to gain a better understanding of the influence of the surface on the adsorbed molecules. From this we can conclude that for the molecular arrangement the molecule-molecule interactions are dominant. However, the stronger molecule-substrate interaction for metal substrates compared to the weakly interacting HOPG was found to lead to a new structure with an alternating rotation of the molecules relative to the lattice vectors.

O 89.3 Fri 11:00 A 053

**Self-assembly of Tetrathiafulvalene-Fused Dipyridophenazine (TTF-dppz) analyzed by tuning fork based AFM/STM** — •SWEETLANA FREMY<sup>1</sup>, RÉMY PAWLAK<sup>1</sup>, SHIGEKI KAWAI<sup>1</sup>, SHI-XIA LIU<sup>2</sup>, SILVIO DECURTINS<sup>2</sup>, ERNST MEYER<sup>1</sup>, and THILO GLATZEL<sup>1</sup> — <sup>1</sup>Department of Physics, University of Basel, Klingelbergstrasse 82, CH-4056 Basel, Switzerland — <sup>2</sup>Department of Chemistry, University of Bern, Freie Strasse 3, CH-3012 Bern, Switzerland

A main challenge of molecular electronics consists in controlling the self-assembly on a surface, which is a highly complex dynamic process with competing binding modes (molecule-surface and intermolecular interactions), driven by thermodynamic and kinetic selectivity. Here, we investigate the self assembly of TTF-dppz molecules (Tetrathiafulvalene-Fused Dipyridophenazine) on metal substrates and insulating thin films by combined tuning fork based atomic force and scanning tunneling microscopy at low temperature. The molecules are additionally functionalized with cyano-groups to yield in a better surface sticking, especially on insulating substrates. While directly after deposition on Cu(111), the molecules are disordered, post-annealing at 100°C leads to highly ordered self-assemblies of molecular wires, a

network with six-fold symmetry, small crystallites and step edge decorations. Most probably the molecules decompose during the annealing, involving Cu-adatoms. The fact, that TTF-dppz molecules do not form such ordered structures on Ag(111), strengthens our presumption. Further investigations comprise the study of single molecules on thin films and the adsorption of the two single compounds dppz and TTF.

O 89.4 Fri 11:15 A 053

**Supramolecular organization and subsequent interlinking of biphenyl derivatives on metal surfaces** — •FEI SONG<sup>1</sup>, TUAN ANH PHAM<sup>1</sup>, SERPIL BOZ<sup>2</sup>, Umut SOYDANER<sup>3</sup>, MARCEL MAYOR<sup>3</sup>, and MEIKE STÖHR<sup>1</sup> — <sup>1</sup>Zernike Institute for Advanced Materials, University of Groningen, the Netherlands — <sup>2</sup>Department of Physics, University of Basel, Switzerland — <sup>3</sup>Department of Chemistry, University of Basel, Switzerland

The combination of their almost infinite structural diversity and unique self-assembly properties makes molecules ideal building blocks for tailor-made materials [1,2]. However, most of such thermodynamically controlled structures are reversible. Therefore, structures with higher stability and improved conductive properties are essential. In this work, a unique concept to control both the molecular self-assembly and the subsequent intermolecular coupling was utilized through the usage of protecting groups.

Herein, biphenyl derivatives with different protecting groups were synthesized and investigated on Ag(111) with STM and XPS before and after annealing. The protecting groups can be split off during the annealing step and the deprotected monomers were found to interlink into polymeric structures. By careful design of the organic monomers, control over reactivity and the size of polymeric structures is achieved.

- [1] S. Boz et al., *Angew. Chem. Int. Ed.* 48 (2009) 3179
- [2] J. Lobo-Checa, et al., *Science*. 325 (2009) 300

O 89.5 Fri 11:30 A 053

**H-bonding as a tool for engineering 1D and 2D supramolecular structures on surfaces** — •MIHAELA ENACHE<sup>1</sup>, MAFRED MATENA<sup>2</sup>, LAURA MAGGINI<sup>3</sup>, ANNA LLANES-PALLAS<sup>3</sup>, DAVIDE BONIFAZI<sup>3</sup>, THOMAS JUNG<sup>2</sup>, and MEIKE STÖHR<sup>1</sup> — <sup>1</sup>University of Groningen, Netherlands — <sup>2</sup>University of Basel, Switzerland — <sup>3</sup>University of Namur, Belgium

By utilizing the concepts of supramolecular chemistry, remarkable results for molecular self-assembly on surfaces have been presented. The outcome of the self-assembly process is known to be affected by the fine tuning of different parameters (such as thermal energy, ratio between different molecular units, etc.) which have a direct influence on the interplay between intermolecular and molecule-substrate interactions.

Herein, we present a scanning tunneling microscopy study demonstrating that - by choosing the recognition moieties appropriately - H-bond recognition between specially designed molecules can predictably lead to the formation of 1D and 2D structures.

Upon adsorption on Ag(111), two different molecular modules self-assemble through triple H-bonding between their complementary recognition moieties forming supramolecular architectures. Depending on the sample preparation parameters, either chain-like or porous structures can be obtained. Therefore, a well-known concept from supramolecular chemistry can be transferred for the fabrication of surface-mounted organic assemblies.

- [1] Llanes Pallas et al., *Angew. Chem. Int. Ed.* 47 (2008) 7726
- [2] Matena et al., *Chem. Commun.* (2009) 3525

O 89.6 Fri 11:45 A 053

**The metal/ionic liquid interface: Structure formation and temperature dependent behavior of ionic liquid adlayers on Au(111)** — •BENEDIKT UHL, MICHAEL ROOS, and ROLF JÜRGEN BEHM — Ulm University, Institute of Surface Chemistry and Catalysis, D-89069 Ulm, Germany

Ionic liquids (IL) are promising electrolytes in Li-Ion batteries. The behavior of the IL's at the electrode surface and the properties of the solid-liquid-interface is crucial for the performance of such electrochemical systems, but investigations on this topic are at their very beginning. In this work, we investigated the structure formation during submonolayer growth of the model systems 1-butyl-1-

methylpyrrolidinium-bis(trifluoromethylsulfonyl)imide (BMP-TFSA) and 1-ethyl-3-methylimidazolium-bis(trifluoromethylsulfonyl)imide (EMIM-TFSA) on Au(111). The resulting structures were characterized with scanning tunneling microscopy (STM) under UHV conditions at temperatures between 100 K and 298 K and at varying IL coverages in the submonolayer regime. At room temperature, the adsorbed IL's form a 2D liquid. At lower temperatures, mobility is frozen and different structures appear. A 2D glassy state and various structures with long range order are detected, depending on the temperature of the substrate during the evaporation process. The 2D crystal structures are influenced by the subjacent Au(111) reconstruction pattern. In addition, the dynamics of the adlayers are investigated during continuous heating from 100 K to room temperature in order to get insight into the thermal stability of the adlayers.

O 89.7 Fri 12:00 A 053

**Hierarchic Formation and Dynamics of Bi-component Supramolecular Networks** — •W. KRENNER<sup>1</sup>, F. KLAPPENBERGER<sup>1</sup>, N. KEPČIJA<sup>1</sup>, E. ARRAS<sup>1</sup>, Y. MAKOUDI<sup>1</sup>, D. KÜHNE<sup>1</sup>, S. KLYATSKAYA<sup>2</sup>, M. RUBEN<sup>2,3</sup>, A. P. SEITSONEN<sup>4</sup>, and J. V. BARTH<sup>1</sup> — <sup>1</sup>Physikdepartment E20, TU München — <sup>2</sup>Institute of Nanotechnology, Karlsruhe Institute of Technology — <sup>3</sup>IPCMS-CNRS UMR 7504, Université de Strasbourg — <sup>4</sup>Physikalisch-Chemisches Institut, Universität Zürich

In this work, the formation and dynamics of bi-component organic molecular networks providing open pores following hierarchic assembly principles are investigated via low- and variable temperature STM in UHV and DFT modeling. By co-depositing N,N' diphenyl oxalic amide (DOA) and sexiphenyl dicarbonitrile (6DC) on Ag(111), self-assembled structures are encountered where organisation depends on the stoichiometric ratio of the constituents.

All network types reflect hierarchic architectures, where similar, essential molecular binding motifs prevail. The different energetics of the individual binding motifs are assessed by theoretical simulation, showing that hierarchic assembly is driven by the strength of the respective interactions. Thereby, the experimentally observed preference of DOA-6DC binding is rationalized, accounting for the formation of mixed phases over phase segregation.

The analysis of the dynamics in the network phase with high variation in binding energies shows good accordance for the diffusion behavior expected from DFT binding energy modeling.

O 89.8 Fri 12:15 A 053

**Structure and Binding of Large Molecules at Metal Surfaces: theoretical NEXAFS for Co-OEP on Ni(100)** — •CHUNSHENG GUO<sup>1</sup>, LILI SUN<sup>1</sup>, KLAUS HERMANN<sup>1</sup>, CHRISTIAN HERMANN<sup>2</sup>, and WOLFGANG KUCH<sup>2</sup> — <sup>1</sup>Theory Department, Fritz-Haber-Institut, Berlin — <sup>2</sup>Inst. of Experimental Physics, Free University, Berlin, Germany

Metal octaethylporphyrins (M-OEP), M-N<sub>4</sub>C<sub>2</sub>O<sub>4</sub>(C<sub>2</sub>H<sub>5</sub>)<sub>8</sub>, adsorbed on metallic substrate are promising candidates to provide spin dependent electric transport. While experimental studies on these systems have been performed details of the adsorbate geometry and surface binding are still unclear. We have carried out density-functional theory (DFT) calculations on free Co-OEP and for Co-OEP adsorbed at Ni(100) with periodic surface models. The resulting equilibrium geometries are then applied in StoBe cluster calculations to yield theoretical C and N 1s excitation spectra of free and adsorbed Co-OEP. Experimental carbon K edge NEXAFS spectra of separate Co-OEP show a triple-peak structure which can be explained from theory by differently binding carbon. When adsorbed at Ni(100) substrate the

triple-peak structure reduces to a double-peak, not yet confirmed by experiment. The measured nitrogen K edge spectra of Co-OEP, showing a double-peak structure, are also affected by the substrate. This is explained by hybridization of adsorbate final state orbitals near the nitrogen centers with 3d orbitals of the Ni substrate due to adsorbate-substrate binding. Test test Test test Test test Test test Test test

Supported by SFB 658 "Molecular switches at surfaces", Berlin

O 89.9 Fri 12:30 A 053

**Evaluation of Degree of Charge Transfer in Classical and Novel Donor-Acceptor Complexes Based on Tetracyanoquinodimethane by HAXPES** — •KATERINA MEDJANIK<sup>1</sup>, ANDREI GLOSKOVSKI<sup>2</sup>, DMYTRO KUTNYAKHOV<sup>1</sup>, CLAUDIA FELSER<sup>2,3</sup>, JEAN-PAUL POUGET<sup>4</sup>, DENNIS CHERCKA<sup>5</sup>, MARTIN BAUMGARTEN<sup>5</sup>, KLAUS MÜLLEN<sup>5</sup>, and GERD SCHÖNHENSE<sup>1</sup> — <sup>1</sup>Inst. für Physik, Univ. Mainz — <sup>2</sup>Inst. für Anorg. und Anal. Chemie, Univ. Mainz — <sup>3</sup>MPI für Chemische Physik fester Stoffe, Dresden — <sup>4</sup>Université Paris-Sud, Orsay, France — <sup>5</sup>MPI für Polymerforschung, Mainz

Combination of the classical acceptor tetracyanoquinodimethane (TCNQ) with novel donors tetra- and hexamethoxyprene (TMP and HMP) can clarify the question about the nature and degree of charge transfer (CT) and give us the possibility to compare the results with measurements and the same conditions for the prototype system TTF-TCNQ. Hard X-ray photoemission (HAXPES) experiment has been performed at PETRA III (beamline P09) on microcrystals and thin films of HMP/TMP-TCNQ. Upon complex formation, we observed a change of the O1s and N1s spectra from a single-line spectrum to a spectrum with two distinct lines shifted by up to 2.6 eV with respect to the position of the line of the pure donors and acceptors. Peak-area analysis reveals a degree of CT of about 0.6e. This value lies close to the CT of 2/3 for TTF-TCNQ estimated by analysis of the sulphur 2p spectra and for similar CT compounds such as NMP-TCNQ [1].

Funding DFG/TR49, Graduate School MAINZ, COMATT.

[1] J. P. Pouget et al., Phys. Rev. B 21 (1980) 486.

O 89.10 Fri 12:45 A 053

**X-ray induced reversible switching of azobenzene derivatives, adsorbed on Bi(111)** — •ALEX KRÜGER, MATTHIAS BERNIEN, CH. FELIX HERMANN, and WOLFGANG KUCH — Freie Universität Berlin, Institut für Experimentalphysik, Arnimallee 14, 14195 Berlin

The adsorption of the photoswitch dimetacyano-azobenzene (DMC) on Bi(111) after deposition at 110 K was studied for different coverages by angle-dependent near-edge x-ray absorption fine structure (NEXAFS) spectroscopy. For the adsorption of one monolayer of molecules we find the molecules physisorbed in a nearly planar conformation parallel to the surface. By illumination with intense x rays two orders of magnitude higher in flux density than used for the NEXAFS measurements at a photon energy corresponding to the azo N 1s → LUMO transition at 399 eV, the angle dependence of the π\* resonances of N-K as well as C-K NEXAFS spectra changes significantly. The effect can be interpreted as a switching of at least 20% of the DMC molecules from the *trans* to the *cis* conformation. The process is reversible, as the NEXAFS spectra become identical to the spectra before the illumination after waiting for 1 h in darkness at 110 K, indicating a thermally induced back reaction. Using off-resonant x rays with an energy of 270 eV for the illumination, no modifications of the NEXAFS N-K and C-K spectra were observed. A comparable effect with an even higher percentage of switched molecules occurs also in multilayers of DMC molecules on Bi(111).

This work is supported by the DFG through Sfb 658.