

## O 42: Organic/bio Molecules on Metal Surfaces IV

Time: Wednesday 10:30–13:15

Location: H38

O 42.1 Wed 10:30 H38

**Modification of Cu(111) with buckybowl** — ●QUIRIN S. STÖCKL<sup>1</sup>, TOBIAS BAUERT<sup>1</sup>, DAVIDE BANDERA<sup>2</sup>, MANFRED PARSCHAU<sup>1</sup>, JAY S. SIEGEL<sup>2</sup>, and KARL-HEINZ ERNST<sup>1,2</sup> — <sup>1</sup>Empa, Nanoscale Material Science, Dübendorf, Switzerland — <sup>2</sup>Organisch-chemisches Institut, Universität Zürich, Switzerland

Interesting candidates for surface modifications for organic photovoltaics or controlled carbon nanotube growth are buckybowl, geodesic polyarenes and quasi-fragments of C<sub>60</sub>. Corannulene (COR, C<sub>20</sub>H<sub>10</sub>) is the simplest curved fragment with a central pentagonal ring, surrounded by five aromatic C<sub>6</sub> rings. Fivefold symmetry is incompatible with the translational order in all 17 plane groups, and this system is therefore of fundamental interest for 2D self-assembly. We have studied therefore the self-assembly of the star-like pentaphenyl-corannulene (Ph<sub>5</sub>Cor) with STM. The packing motifs basically consist of anti-parallel rows with interdigitated substituents. Results will be compared to structures found for other penta-substituted COR derivatives and for monoindeno-corannulene.

O 42.2 Wed 10:45 H38

**C<sub>58</sub> on Au(111): an STM-based study** — NOELIA BAJALES<sup>1</sup>, STEFAN SCHMAUS<sup>1</sup>, TOSHIO MIYAMACHI<sup>1</sup>, WULF WULFHEKEL<sup>1</sup>, JAN WILHELM<sup>2</sup>, MELANIE STENDEL<sup>2</sup>, MICHAEL WALZ<sup>2</sup>, ALEXEJ BAGRETS<sup>2</sup>, FERDINAND EVERS<sup>2</sup>, SEYITHAN ULAS<sup>3</sup>, ●BASTIAN KERN<sup>1,3</sup>, ARTUR BÖTTCHER<sup>3</sup>, and MANFRED M. KAPPES<sup>3</sup> — <sup>1</sup>Institute of Physics, Karlsruhe Institute of Technology (KIT), Wolfgang-Gaede-Str. 1, D-76131 Karlsruhe, Germany — <sup>2</sup>Institute of Nanotechnology, Karlsruhe Institute of Technology (KIT), Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany — <sup>3</sup>Institute of Physical Chemistry, Karlsruhe Institute of Technology (KIT), Fritz-Haber-Weg 2, 76131 Karlsruhe, Germany

Non-IPR C<sub>58</sub> cages were adsorbed at room temperature onto Au(111) by low-energy cluster beam deposition (E<sub>kin</sub> 6 eV [1]). The surface topography and electronic properties of the system were investigated with a 4K-STM. The topographic images reveal that in the early adsorption stage (i.e. at low coverages), the cages are pinned by step edges and dislocation point defects and act as nucleation centers for growth of 2D islands. The isolated monomers exhibit no internal structure due to covalent bonding to the Au(111) surface. The short oligomers reflect a spontaneous surface-mediated polymerization of the cages. Dimers and trimers exhibit unique topographic features which reveal the covalent nature of the intercage bonds. The surface-independent outermost C<sub>58</sub> layers appear to be wide band semiconductors (HOMO-LUMO gap 1.2 eV). Experimental results are compared with detailed DFT calculations.

O 42.3 Wed 11:00 H38

**The molecular structure of a nine amino acid peptide at metal surfaces in vacuum** — ●GORDON RINKE<sup>1</sup>, STEPHAN RAUSCHENBACH<sup>1</sup>, RICO GUTZLER<sup>1</sup>, ALYAZAN ALBARGASH<sup>1</sup>, LUDGER HANAU<sup>2</sup>, and KLAUS KERN<sup>1,3</sup> — <sup>1</sup>Max-Planck Institute for Solid State Research, Stuttgart, Germany — <sup>2</sup>Max-Planck Institute for Intelligent Systems, Stuttgart, Germany — <sup>3</sup>Institut de Physique de la Matière Condensée, EPF Lausanne, Switzerland

Self-assembly of small molecules at surfaces in ultrahigh vacuum (UHV) is typically described as the interplay of intermolecular and molecule-surface interactions. Significant conformational changes or intramolecular interactions are rarely considered in this picture of self-assembly because these are relevant only for large molecules, which cannot be brought to surfaces in UHV by conventional deposition methods. The combination of electrospray ion beam deposition and scanning tunneling microscopy (STM) allowed us to study the molecular self-assembly of proteins and peptides in UHV.

In this study we address the self-assembly of Bradykinin (BK), a nine amino acid peptide with a mass of 1060u and large enough to interact with itself. Experimentally we find several conformations of BK in single molecule and dimer structures as well as in a superstructure of dimers. Conformations suggested by molecular dynamics simulations and calculated by density functional theory are compared to STM topographies and provide a tentative model of the adsorption.

Our study suggests that rationally synthesized peptides on surfaces can fold into structures with unique catalytic and chemical functions.

O 42.4 Wed 11:15 H38

**Specific Material Binding by Peptide Motifs on the Oxidized Titanium and Silicon Surface** — ●JULIAN SCHNEIDER<sup>1,2</sup> and LUCIO COLOMBI CIACCHI<sup>1</sup> — <sup>1</sup>Hybrid Materials Interfaces Group, Bremen Center for Computational Materials Science, University of Bremen, Germany — <sup>2</sup>Department Chemie, Technical University Munich, Germany

The specific recognition of materials surfaces by small peptide sequences has become a widely investigated, interdisciplinary research topic with fields of application ranging from bio-nanotechnology to medicine and pharmacology [1]. However, a rationalization of the binding driving forces in terms of a clear structure-function relationship is missing, as the atomistic details of material surfaces in a wet environment are hard to elucidate both experimentally and theoretically.

Using a combination of metadynamics, replica exchange and steered molecular dynamics simulations we unveil the origin of the selectivity of specific binding motifs for Ti over Si, obtaining adsorption free energies and adhesion forces in quantitative agreement with corresponding experiments. We present evidence that the observed material recognition by small peptides is governed by local solvent density variations at solid/liquid interfaces, sensed by the side-chain residues with atomic-scale precision [2].

[1] M. Sarikaya, C. Tamerler, A. K.-Y. Jen, K. Schulten, and F. Baneyx. *Nature Mater.*, **2**, 577 (2003).

[2] J. Schneider and L. Colombi Ciacchi. *J. Am. Chem. Soc.* **134**, 2407 (2012).

O 42.5 Wed 11:30 H38

**Chemical Transformations of Bisphenol A on Cu(111) and Ag(111)** — ●JULIAN LLOYD, SYBILLE FISCHER, ANTHOULA PAPA-GEORGIOU, MATTHIAS MARSCHALL, JOACHIM REICHERT, KATHARINA DILLER, FLORIAN KLAPPENBERGER, FRANCESCO ALLEGRETTI, and JOHANNES V. BARTH — Physik Department E20, TUM, Garching

Bisphenol A (BPA) is a common additive to everyday polymers and its suspected adverse health effects led to its EU ban from use in baby bottles in June 2011. Some of these effects are traced to DNA alterations [1]. The reactivity of BPA has not been reported in a systematic way and the key molecular events and interactions driving the self-assembly of non-coplanar phenols have hitherto not been addressed unambiguously by a combinatorial approach of microscopy and spectroscopy. In this study we address the chemical transformations of BPA on transition and noble metal surfaces, copper and silver. These transformations are expected to induce changes in the surface self-assembly. Performing a scanning tunneling microscopy study of BPA on a Cu(111) and a more inert Ag(111) surface we observed multiple extended two dimensional networks dependent on temperature and substrate metal. To further elucidate the chemical state and the orientation of the molecule in the aforementioned phases, we performed synchrotron X-ray photoelectron spectroscopy and near-edge X-ray absorption fine structure studies. We find a complex, stepwise deprotonation scheme mediating the structural transformations. Based on the data sets we present a simple comprehensive model of the observed phases.

[1] D.C. Dolinoy, et. al. PNAS 104, 13061 (2007).

O 42.6 Wed 11:45 H38

**Diethylstilbestrol on Ag(111) and Cu(111): an STM study** — ●SEUNG CHEOL OH, JULIAN A. LLOYD, SYBILLE FISCHER, ÖZGE ALTUNTASOGLU SAGLAM, ANTHOULA C. PAPA-GEORGIOU, JOACHIM REICHERT, and JOHANNES V. BARTH — Physik Department E20, Technische Universität München, 85748 Garching, Germany

Diethylstilbestrol (DES) is a synthetic estrogen, which has been banned after its association with adverse health effects. It contains two phenol groups, which can be coplanar, thus allowing the molecule to act as ditopic surface molecular linker. Our study was motivated by the fact that phenol groups can be used to control of molecular self-assembly [1]. Here we focus on investigating the self-assembly of DES on two single crystal metal surfaces by means of variable-temperature scanning tunneling microscopy (STM). We find a variety of different two-dimensional molecular networks depending on the supporting metal (silver and copper) and on the annealing temperature. Based on the known interactions of phenols on surfaces as well as a

careful analysis of STM topographic images we present tentative structural models for the observed self-assembled nanostructures.

[1] Pawlak, R. et al. *ChemPhysChem* **2009**, *10*, 1032–1035.

O 42.7 Wed 12:00 H38

**Initial growth of quinacridone on Ag(111)** — •THORSTEN WAGNER, MICHAEL GYÖRÖK, DANIEL HUBER, and PETER ZEPPENFELD — Johannes Kepler University, Institute of Experimental Physics, Linz, Austria

The organic dye pigment quinacridone (QAC) may play a role as an outsider in view of record breaking organic semiconductors like rubrene, but its dominant H-bonds might be a key to innovative device structures. Therefore, this work focusses on the initial growth of quinacridone on Ag(111) surfaces at room temperature. During deposition, the local electron yield was monitored in a photoelectron emission microscope (PEEM) showing no spatial inhomogeneities on a scale between 100 nm and 100  $\mu\text{m}$  for up to 5 monolayers. This could be either due to a smooth layer-by-layer growth or the formation of extraordinary small 3D crystallites. The initial increase of the yield can be attributed to a lowering of the work function upon formation of the first monolayer. As the ionization potential of QAC (5.4 eV [1]) is actually higher than the photon energy (4.9 eV), a continuous decrease even below the emission of the bare Ag(111) substrate was observed afterwards. Scanning tunneling microscopy images of the initial layer exhibit a simple, raw-like stacking of parallel molecules which can be explained by hydrogen bonding between adjacent, flat-lying molecules. After annealing to a temperature of  $T=550\text{--}570\text{ K}$ , which is close to the desorption temperature of the multilayer, the structure changes to a stacking of dimers. Additional LEED data support the STM findings.

[1] Glowacki et al. in *Applied Physics Letters* *101*, 023305 (2012)

O 42.8 Wed 12:15 H38

**Different behaviour of Hydrogenated vs. Fluorinated Tribromobenzene on Ag(111) and Cu(111): the influence of pendant groups** — •STEFAN SCHLÖGL<sup>1,2</sup>, WOLFGANG M. HECKL<sup>1,2</sup>, and MARKUS LACKINGER<sup>1,2</sup> — <sup>1</sup>Department of Physics & TUM School of Education, Tech. Univ. Munich, Schellingstrasse 33, 80333 Munich, Germany — <sup>2</sup>Deutsches Museum, Museumsinsel 1, 80538 Munich, Germany

A lot of effort has been put into the realization of the dream of two-dimensional polymers. Bottom-up fabrication of 2D polymers facilitates tailoring of desired electrical, thermal and mechanical properties for new classes of materials and semiconductors.[1] To gain further knowledge about on-surface reactions of 2D polymers, a systematic study of the influence of pendant groups on the self-assembly and polymerization process has been performed. Pendant groups are known to alter physical and electrochemical properties of synthesized polymers.[2] Here we compare the polymerization of *s*-tribromobenzene derivatives either hydrogenated or perfluorinated on two surfaces. Therefore, 1,3,5-Tribromo-2,4,6-Trifluoro-benzene and 1,3,5-Tribromobenzene were deposited onto Ag(111) and Cu(111) and characterized by means of scanning tunneling microscopy under ultra-high vacuum conditions. Reaction mechanisms to describe the different behavior of the two monomers are proposed.

[1] Sakamoto, J. et al., *Angew. Chem., Int. Ed.*, *48* (2009), Nr. 6, 1030-1069. [2] Wang, Z. et al., *J. Membrane Sci.*, *285* (2006), Nr. 1-2, 239-248.

O 42.9 Wed 12:30 H38

**Synthesis of 2D covalent networks through Ullmann coupling of a threefold symmetric hexabrominated molecule** — •ATENA RASTGOO LAHROOD<sup>1,2</sup>, THOMAS SIRTIL<sup>1,2</sup>, WOLFGANG HECKL<sup>1,2</sup>, and MARKUS LACKINGER<sup>1,2</sup> — <sup>1</sup>Department of Physics & TUM School of Education, Tech. Univ. Munich, Schellingstrasse 33, 80333 Munich, Germany — <sup>2</sup>Deutsches Museum, Museumsinsel 1, 80538 Munich, Germany

Over the last few years, 2D covalent materials have gained a lot of interest in different fields of studies because of their extraordinary

properties. One of the common bottom-up synthesis methods for 2D covalent networks is surface mediated polymerization of halogenated organic monomers. Thereby, surface stabilized radicals are generated through the homolysis of carbon-halogen bonds. Subsequent diffusion and radical recombination reactions yield covalently cross-linked networks. In this contribution we will discuss the role of the monomer halogen substitution pattern for the topology and defect density in covalent networks. Moreover, comparative studies on densely packed coinage metal surfaces (Cu(111), Ag(111), Au(111)) and additional thermal treatment reveal the influence of further important parameters. The structures are prepared in ultra-high vacuum and analyzed by STM and LEED. Molecules were also deposited onto Ag(111) and Cu(111) at low temperature and structural changes that hint toward the onset of polymerization were studied as a function of temperature.

O 42.10 Wed 12:45 H38

**Unconventional self-assembled monolayers with unusual properties** — DAVID A. EGGER<sup>1</sup>, FERDINAND RISSNER<sup>1</sup>, OLIVER T. HOFMANN<sup>1</sup>, AMIR NATAN<sup>2,3</sup>, LEEOR KRONIK<sup>2</sup>, GEORG HEIMEL<sup>4</sup>, and •EGBERT ZOJER<sup>1</sup> — <sup>1</sup>Institute of Solid State Physics, Graz University of Technology, 8010 Graz, Austria — <sup>2</sup>Department of Materials and Interfaces, Weizmann Institute of Science, 76100 Rehovoth, Israel — <sup>3</sup>Department of Physical Electronics, 69978 Tel-Aviv University, Tel-Aviv, Israel — <sup>4</sup>Institut für Physik, Humboldt-Universität zu Berlin, Brook-Taylor-Straße 6, 12489 Berlin, Germany

We use density-functional theory calculations to show that self-assembled monolayers (SAMs) made from molecules consisting of conjugated distributed dipolar units have unusual properties: \* Work-function modifications tuned linearly with the number of repeat units are limited by Fermi-level pinning,[1] where the limitations can be overcome using advanced design strategies.[2] \* Collectively induced internal electric fields change the nature of the electronic states within such SAMs in a way strongly reminiscent of the quantum-confined Stark-effect [3] with a closure of the global band-gap beyond a certain number of repeat units. [4] \* Moreover, SAMs can be realized that display different polarity of charge transport, in spite of consisting of molecules with virtually identical electronic properties.[5] All these observations can be traced back to collective effects prevalent in such SAMs. [1] *Phys.Chem.Chem.Phys.*, *2010*, *12*, 4291; [2] *Nano Lett.* *10*, 4369 (2010); [3] *J. Am. Chem. Soc.* *133*, 18634 (2011); [4] *Org. El.* *13*, 3165 (2012); [5] *Adv. Mater.* *24*, 4403 (2012).

O 42.11 Wed 13:00 H38

**Control of Intermolecular Bonds by Deposition Rates: Hydrogen Bonds vs. Metal-Coordination in Trinitrile Monolayers** — •THOMAS SIRTIL<sup>1,2</sup>, STEFAN SCHLÖGL<sup>1,2</sup>, ATENA RASTGOO-LAHROOD<sup>1,2</sup>, JELENA JELIC<sup>3</sup>, SUBHADIP NEOGI<sup>4</sup>, MICHAEL SCHMITTEL<sup>4</sup>, WOLFGANG M. HECKL<sup>1,2,5</sup>, KARSTEN REUTER<sup>3</sup>, and MARKUS LACKINGER<sup>2,5</sup> — <sup>1</sup>Department of Physics, Tech. Univ. Munich, James-Franck-Str. 1, 85748 Garching — <sup>2</sup>Center for NanoScience (CeNS), Schellingstr. 4, 80799 Munich — <sup>3</sup>Department of Chemistry, Tech. Univ. Munich, Lichtenbergstr. 4, 85747 Garching — <sup>4</sup>Center of Micro- and Nanochemistry and Engineering, Organische Chemie I, Universität Siegen, Adolf-Reichwein-Str. 2, 57068 Siegen — <sup>5</sup>Deutsches Museum, Museumsinsel 1, 80538 Munich (all Germany)

Self-assembled monolayers of a large functional trinitrile molecule are studied on the (111) surfaces of copper and silver by scanning tunneling microscopy (STM) and low energy electron diffraction (LEED). A densely packed hydrogen bonded polymorph was equally observed on both surfaces. Additionally, deposition onto Cu(111) yielded a well-ordered metal-coordinated porous polymorph that coexisted with the hydrogen bonded structure. The coordination centers are supplied by the adatom gas of Cu(111). On Ag(111) the metal-coordinated network was never observed. Differences in the adatom reactivity and the resulting bond strength are held responsible for this substrate dependence. By utilizing ultra-low deposition rates, we demonstrate that on Cu(111) adatom kinetics plays a decisive role in the expression of intermolecular bonds - and hence for structure selection.