

## O 86: Nanostructure at Surfaces: Molecular Assembly

Time: Thursday 15:00–17:45

Location: HE 101

## Invited Talk

O 86.1 Thu 15:00 HE 101

**On-surface synthesis of molecular and polymeric nanostructures** — ●J. MICHAEL GOTTFRIED — Fachbereich Chemie, Philipps-Universität Marburg, Hans-Meerwein-Straße 4, 35032 Marburg, Germany

The on-surface synthesis of organic molecules, organometallic compounds, and two-dimensional polymeric networks is an increasingly popular field of study in surface science and holds promise as an approach for surface modification and functionalization. Surface reactions in ultrahigh vacuum can produce novel molecular compounds which are not accessible by conventional synthesis in solution or which are too large or too reactive for vapor deposition. Catalytic and template effects exerted by the surface can help driving the reaction into the desired direction. In this contribution, recent advances in the on-surface synthesis of large molecular species and two-dimensional polymeric structures will be reviewed. Prominent examples include conjugated hydrocarbon macrocycles such as hyperbenzene and its homologues, which are synthesized by the surface-assisted Ullmann reaction. This reaction also provides access to cyclic and linear organometallic structures. Related topics that will be covered include strategies for the synthesis of low-defect covalent networks through the on-surface synthesis of suitable molecular building blocks and the role of side products for structure formation.

O 86.2 Thu 15:30 HE 101

**Tuning on-surface coordination polymers to form chains and networks forming quantum boxes to investigate Xe condensation in an atom-by-atom manner.** — ●O. POPOVA, S. NOWAKOWSKA, A. WÄCKERLIN, S. KAWAI, T. IVAS, J. NOWAKOWSKI, S. FATAYER, C. WÄCKERLIN, T. NIJS, J. GIROVSKY, S. MARTENS, A. KLEIBERT, N. BALLAV, E. MAYER, J. BJÖRK, M. STÖHR, L. GADE, and T. JUNG — Basel, Switzerland

Coordination between organic molecular ligands and metal adatoms has been established to form stable, well-ordered and here chemically tunable endo or exo-ligands and corresponding polymers. By combining STM, XPS, NEXAFS and DFT, we demonstrate that the amino-functionalized perylene derivative, DPDI, undergoes specific levels of dehydrogenation depending on the nature of the present adatoms. Moreover, the Cu-coordinated 3deh-DPDI network which is created after the deposition of DPDI on Cu(111) and subsequent annealing confines the Shockley surface state into well-defined quantum boxes. These boxes provide an ideal template for studying Xe condensation process atom-by-atom under the interplay of different well known interactions. Our direct, real-space analysis reveals the subtle interplay of competing directional and non-directional interactions which determine the condensate structure. This approach is applicable significantly beyond the presented Xe case. Also such adsorbate containing \*quantum boxes\* provide unprecedented systems for the in-depth comparison of simulations using different quantum mechanical models.

O 86.3 Thu 15:45 HE 101

**Self-assembly of NC-Ph3-CN molecules on Cu(111): an unusual alignment with respect to the substrate** — ●GIULIA E. PACCHIONI, MARINA PIVETTA, and HARALD BRUNE — Ecole Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland.

The self-assembly of dicyanide polyphenyl molecules (NC-Ph<sub>3</sub>-CN) on metal surfaces is a widely studied subject. These molecules on Ag(111) are in most cases aligned along the first or second nearest neighbors directions of the substrate. For NC-Ph<sub>5</sub>-CN molecules on Cu(111) the alignment along the second nearest neighbors is the only one observed. On Cu(111) the alignment along this direction is particularly favorable, since it allows an almost perfect epitaxial fit of the molecules with respect to the substrate. The behavior of NC-Ph<sub>3</sub>-CN molecules on Cu(111) is in this respect rather bizarre: while for purely organic assemblies the alignment is, as expected, along the high symmetry directions, when the network is metal coordinated the molecules align along a bunch of directions deviating from the second nearest neighbors ones by 4, 11 and 18 degrees. The resulting networks have a strongly reduced degree of order compared to NC-Ph<sub>5</sub>-CN on Cu(111) assemblies. We explain this peculiar behavior through the interplay between the gain in energy obtained by forming a straight CN-Cu bond at the molecule ends, and the one given by having the

hydrogen and nitrogen atoms placed on favorable adsorption sites on the surface. We show that these two preferences cannot be satisfied at once, so depending on the length of the molecule one or the other will prevail, giving rise to different dispositions on the substrate.

O 86.4 Thu 16:00 HE 101

**Surface mediated synthesis of metal-organic architectures based on thiolate-gold coordination bonds** — ●ATENA RAST-GOO LAHROOD<sup>1,2</sup>, MATTHIAS LISCHKA<sup>1,2</sup>, JOHANNA EICHHORN<sup>1,2</sup>, THOMAS STRUNSKUS<sup>1</sup>, WOLFGANG M. HECKL<sup>1,2,3</sup>, and MARKUS LACKINGER<sup>1,2,3</sup> — <sup>1</sup>Department of Physics, Technische Universität München, Germany — <sup>2</sup>Center for NanoScience (CeNS), Munich, Germany — <sup>3</sup>Deutsches Museum, Munich, Germany — <sup>4</sup>Institute for Materials Science - Multicomponent Materials, CAU, Kiel, Germany

In our previous work we studied self-assembly of 1,3,5-tris(4-mercaptophenyl)benzene on Cu(111) and Ag(111). Upon room temperature deposition, densely packed structures were found that could subsequently be converted into more complex and open structures by mild annealing. On Cu(111) two different metal coordinated structures could be identified. To shine more light on the substrate influence further studies were carried out on Au(111). Contrary to copper and silver surfaces the initial densely packed structure was never observed. In contrast, already after room temperature deposition we observed a variety of less well-ordered structures that could be identified as metal-coordinated based on bond geometry and XPS data. Post annealing of the surface in successive steps led to the emergence of better ordered likewise metal-organic aggregates and networks with a dominance of distinct motifs at specific temperatures. Even higher annealing temperatures eventually result in sulphur cleavage and disordered molecular structures. All the samples were prepared and analyzed (STM, XPS and NEXAFS) in an UHV chamber.

O 86.5 Thu 16:15 HE 101

**A predictive model for the self-assembly of organic molecules on weakly interacting surfaces** — ●JOOST VAN DER LIT<sup>1</sup>, JOLIEN MARSMAN<sup>2</sup>, NADINE J. VAN DER HEIDEN<sup>1</sup>, STEPHAN DEN HARTOG<sup>1</sup>, PETER H. JACOBSE<sup>1</sup>, ROBERTUS J.M. KLEIN GEBBINK<sup>3</sup>, LAURA C. FILION<sup>2</sup>, and INGMAR SWART<sup>1</sup> — <sup>1</sup>Condensed Matter and Interfaces, Debye Institute for Nanomaterials Science, Utrecht University, The Netherlands — <sup>2</sup>Soft Condensed Matter, Debye Institute, Utrecht University, The Netherlands — <sup>3</sup>Organic Chemistry and Catalysis, Debye Institute, Utrecht University, The Netherlands

Two-dimensional crystals of organic molecules on surfaces are highly attractive for applications ranging from molecular electronics to gas sensors to protective coatings[1]. The geometry of these crystals is an important parameter in determining their functionality. However, currently there is no model available that can be used to a-priori predict what crystal structures will form.

We developed a model, based on electrostatic and van der Waals interactions, that is capable of predicting the ordering of molecules on weakly interacting metal surfaces. Using scanning tunneling microscopy and atomically resolved atomic force microscopy, we studied the self-assembly of two different molecules on Au(111). These bis-acetylene molecules form different crystal structures. Our model correctly reproduces the two different crystal structures that we see experimentally. Additionally, we accurately reproduce the crystal structure of molecules whose self-assembly has been reported in literature.

1. L. Bartels, Nat. Chem., 2, 87-95, (2010)

O 86.6 Thu 16:30 HE 101

**Ethene to graphene: surface catalyzed chemical pathways, intermediates, precursors, and assembly** — BO WANG<sup>1</sup>, MICHAEL KÖNIG<sup>1</sup>, CATHERINE J. BROMLEY<sup>2</sup>, BOKWON YOON<sup>3</sup>, ●FRIEDRICH ESCH<sup>1</sup>, ULRICH HEIZ<sup>1</sup>, UZI LANDMAN<sup>3</sup>, and RENALD SCHAUB<sup>2</sup> — <sup>1</sup>Chemistry Dept., Technische Universität München, Catalysis Research Center, 85748 Garching, Germany — <sup>2</sup>EaStCHEM and School of Chemistry, University of St Andrews, St Andrews, KY16 9ST, United Kingdom — <sup>3</sup>School of Physics, Georgia Institute of Technology, Atlanta, Georgia 30332-0430, USA

Diverse technologies, from catalyst coking to graphene synthesis, entail hydrocarbon dehydrogenation and condensation reactions on transition metal surfaces and assembly into carbon overlayers. Scanning-

tunneling microscopy (STM), thermal-desorption spectroscopy (TDS), and density-functional theory (DFT) simulations were used to uncover the hierarchy of atomic-scale pathways and reaction intermediates underlying the catalyzed thermal evolution of ethene adsorbed on Rh(111) to form 2D graphene overlayers:

Upon heating, adsorbed ethene molecules evolve at first via coupling reactions to form segmented 1D polyaromatic hydrocarbon chains. Further heating leads to dimensionality-crossover (1D to 2D) and dynamical restructuring processes at the PAH chain-ends, with subsequent activated detachment of 24-carbon-atom dehydrogenated-coronene-like clusters. Rate-limiting diffusional coalescence of these dynamically self-evolved precursors culminates at even higher temperatures (1000 K) in condensation into a graphene adlayer of high structural perfection.

O 86.7 Thu 16:45 HE 101

**A strategy for surface grafting of covalent networks: a combined STM, NEXAFS, and XPS study of Ullmann coupling of a fluorinated precursor** — ●MATTHIAS LISCHKA<sup>1,2</sup>, JOHANNA EICHHORN<sup>1,2</sup>, ATENA RASTGOO-LAHROOD<sup>1,2</sup>, THOMAS STRUNSKUS<sup>3</sup>, ROCHUS BREUER<sup>4</sup>, MICHAEL SCHMITTEL<sup>4</sup>, WOLFGANG M. HECKL<sup>1,2,5</sup>, and MARKUS LACKINGER<sup>1,2,5</sup> — <sup>1</sup>Department of Physics, Technische Universität München, James-Frank-Str. 1, 85748 Garching — <sup>2</sup>Center for NanoScience (CeNS), Schellingstr. 4, 80799 Munich — <sup>3</sup>Institute for Materials Science - Multicomponent Materials, Christian-Albrechts-Universität zu Kiel, Kaiserstr. 2, 24143 Kiel — <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

Thermally activated surface chemistry of tetrabromohexafluorobiphenyl on Ag(111) is studied under ultrahigh vacuum conditions by a range of surface sensitive techniques. X-ray photoelectron spectroscopy of C 1s, Br 3d, and F 1s was used to identify chemical changes that indicated the occurrence of three distinct phases. Upon progressive heating, an initial partly organometallic phase becomes fully organometallic, and is eventually converted into a covalent network. The structural characterization of each phase is carried out by a combination of high resolution scanning tunneling microscopy and C 1s near edge x-ray absorption fine structure. The latter offers detailed insights into the orientation of the phenyl rings with respect to the surface.

O 86.8 Thu 17:00 HE 101

**Structure formation of lipophilic molecules on surfaces in a non-equilibrium setting: A computational study** — ●PRITAM KUMAR JANA and ANDREAS HEUER — Institute for physical chemistry, University of Muenster, Germany

Recently, the group of Prof. Chi (Muenster) has observed that N9-substituted adenine derivative in solution form two different type of structures (intercalation vs. stripes patterns) on the surface[1]. Extending that study to deposition experiments, information about the impact of deposition rate and substrate temperature on structure formation has been obtained [2]. It has been observed that higher deposition rates and lower substrate temperatures prefer to stabilize the intercalated structure. We present kinetic Monte Carlo simulations where the molecules are represented as model chains with one head-type and a few tail-type monomers. The key interaction properties, i.e., the formation of hydrogen bonds (intercalated structure) and pi-pi interactions (stripe interaction) among the adenine molecules, respectively, and the van der Waals chain-chain interactions, are reflected in

this model, based on DFT-based parameters. The quality of structure formation in dependence on deposition rate and substrate temperature as well as the relative fraction of both phases is analysed and compared with experimental data. Good qualitative agreement is achieved.

[1] Mu et al. Langmuir, 29, 10737, 2013

[2] Wang et al. Chem. Comm., 50, 9192, 2014

O 86.9 Thu 17:15 HE 101

**Reversible photoisomerization within monolayers of a  $\pi$ -expanded oligothiophene 8-mer: A photosensitive molecular cargo nanoarchitecture** — ●JOSE D. COJAL<sup>1</sup>, MASAHIKO IYODA<sup>2</sup>, and JÜRGEN P. RABE<sup>1</sup> — <sup>1</sup>Department of Physics & IRIS Adlershof, Humboldt-Universität zu Berlin, Berlin, Germany — <sup>2</sup>Department of Chemistry, Tokyo Metropolitan University, Tokyo, Japan

A  $\pi$ -expanded oligoethynylene-thiophene macrocycle has been optically switched between its *E,E*- and *Z,Z*-conformers in different solutions. Here, we report a self-assembled monolayer of *Z,Z*-8mer (*E,E*-8mer) between its octanoic acid solution and HOPG, which upon illumination at 365nm (550nm) with an intensity of  $\sim 1\text{mW}/\text{cm}^2$ , photoisomerizes to the *E,E*-8mer (*Z,Z*-8mer). The switching process was followed using STM imaging while irradiating with the corresponding wavelength. The 2D-hexagonal network of the *Z,Z*-8mer displayed an average unit cell of  $a=(2.76\pm 0.01)\text{nm}$ ,  $b=(2.86\pm 0.03)\text{nm}$ ,  $\theta=(60.8\pm 0.8)^\circ$ , while the *E,E*-8mer exhibited a different average unit cell  $a=(2.89\pm 0.02)\text{nm}$ ,  $b=(2.95\pm 0.03)\text{nm}$ ,  $\theta=(60.3\pm 0.8)^\circ$  with a 95% of confidence level. To validate the reversible switching, emission spectra were recorded starting with a monolayer of *Z,Z*-8mer, which isomerizes to the *E,E* form after 15 minutes of illumination at 365nm with an intensity of  $700\text{mW}/\text{cm}^2$ , and returns to the original spectrum after 15 additional minutes of illumination at 550nm with an intensity of  $500\text{mW}/\text{cm}^2$ . Combining the photoswitchable properties of the monolayers of the macrocycle with its host-guest capabilities we envisage a photosensitive molecular cargo system.

O 86.10 Thu 17:30 HE 101

**Selfassembly of organic semiconductor monolayer via solid-solid wetting: physico-chemical basics, controllability, process capability** — ●ALEXANDER EBERLE<sup>1,2,3</sup> and FRANK TRIEXLER<sup>1,2,3</sup> — <sup>1</sup>Earth and Environmental Sciences, Ludwig-Maximilians-Universität München (LMU) — <sup>2</sup>Center for NanoSciences (CeNS) — <sup>3</sup>Deutsches Museum, München, Germany

Organic Solid-Solid Wetting Deposition (OSWD) (Triexler et al.: Chem.Eur.J. 13 (2007), 7785) enables to deposit insoluble molecules such as organic pigments and semiconductors on substrate surfaces such as graphite and graphene under ambient conditions. Important for enabling a broader application of OSWD is the exploration of its potential to easily grow and manipulate monolayers. In the presented study we use Quinacridone as a model system, an organic semiconductor and pigment, which finds extensive use in industrial applications. Results of investigations via Scanning Tunneling Microscopy (STM), particle size distribution and zeta potential analysis are presented which give a deeper insight into the physico-chemical basics, the controllability and the process capability of the OSWD technique. The results explain existing and open up new advantages (cheap and fast process, chemical and mechanical resistance, directed domain growth in micro- and nanoscale, nanomanipulation, co-adsorption), explain restrictions (domain-structure, coverage) and point towards prospective applications (band-gap engineering of graphene, Van der waals heterostructures) of OSWD for surface physics, supramolecular chemistry and carbon-based electronics.