O 87: Focus Session: Molecular Nanostructures on surfaces - New Concepts towards Complex Architectures V

Organizers: Sabine Maier, FAU Erlangen-Nürnberg; Meike Stöhr, University of Groningen

(Synopsis provided with part I of this session)

Time: Thursday 10:30–13:00 Location: MA 004

Invited Talk O 87.1 Thu 10:30 MA 004

Molecular structures for conductance measurements — •Richard Berndt — Christian-Albrechts-Universität zu Kiel, D-24098 Kiel

Switching and spin effects in adsorbed molecules may be addressed by probing their conductances with low-temperature scanning tunneling microscopes. My talk will first cover results from molecules that are brought into ultrahigh vacuum with electrospray. This method is suitable for largish molecules and consequently a degree of complexity may be added to the molecules themselves. In addition, measurements will presented from sublimable molecules that are adsorbed through suitable molecular subunits serving as platforms.

This work was supported by SFBs 668 and 677.

O 87.2 Thu 11:00 MA 004

On-surface molecular synthesis of thermally unaccessible molecules by reactive landing electrospray ion beam deposition. — •Lukas Krumbein[1], Sabine Abb[1], Suman Sen[1], Klaus Kern[1,2], and Stephan Rauschenbach[1,3] — [1]Max-Planck-Institute for Solid State Research, 70569 Stuttgart, Germany — [2]Institut de Physique, École Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland — [3]University of Oxford, Department of Chemistry, OX1 3TA Oxford, UK

On-surface molecular reactions have been in the focus of research due to their potential impact in molecular devices and for robust surface functionalization. Generally those reactions require thermal activation.

Alternatively electrospray ion beam deposition (ES-IBD) provides charged molecular beams for deposition at collision energies freely tunable in the range of 2eV-200eV. A surface collision at this energy is sufficient to drive on-surface reactions at room temperature.

Using the Reichardt's Dye molecule as a model systems we demonstrate equivalent on-surface reactions upon thermal annealing as well as hyperthermal surface collision. In particular we observe the formation of covalently linked dimers and (cyclo-) dehydrogenation including transition states not accessible by thermal annealing.

O 87.3 Thu 11:15 MA 004

Electrospray deposition of a Spoked Wheel molecule on bulk insulator surfaces in UHV — •Sebastian Scherb[1], Antoine Hinaut[1], Akimitsu Narita[2], Klaus Müllen[2], Sara Freund[1], Zhao Liu[1], Thilo Glatzel[1], and Ernst Meyer[1] — [1]Department of Physics, University of Basel, Basel, Switzerland — [2]Max Planck Institute for Polymer Research, Mainz, Germany

Deposition of large, structurally complex molecules in UHV provides interesting prospects for applications in optoelectronics and molecular electronics. With increasing size, complexity or chemical reactivity deposition by thermal evaporation becomes challenging. A possible way to deposit such molecules in clean conditions is electrospray deposition. Since for the study of electronic properties of molecules decoupling from the surface is mandatory, deposition on insulator surfaces is necessary. In previous studies [1] triply fused porphyrin molecules were deposited on the KBr(001) surface, proving the capabilities of electro spray deposition for depositing organic molecules on bulk insulator.

Here, we report the deposition of a shape persistent polyphenylene Spoked Wheel molecule [2] onto KBr(001) using electrospray deposition in UHV. We show island growth on Au(111) and KBr(001) surfaces by ncAFM study in UHV at room temperature. We are further able to provide molecular resolution of islands, observing straight interdigitation of alkyl chains on the Au(111) surface and a tilting of the interdigitating alkyl chains on the KBr(001) surface.

[1] Hinaut, A. et al., Beilstein J. Nanotechnol. 6, 1927-1934 (2015). [2] Liu, Y. et al., J. Am. Chem. Soc. 138, 15539-15542 (2016).

O 87.4 Thu 11:30 MA 004

Self-assembly of synthetic peptides on surfaces — •Uta Schlickum[1,2], Sebastian Koslowski[1], Suman Sen[1], Xu Wu[1], Sabine Abb[1], Stephan Rauschenbach[1], and Klaus Kern[1,3] — [1]Max-Planck-Institut für Festkörperforschung, 70569 Stuttgart, Germany — [2]Institut für Angewandte Physik, TU Braunschweig, 38106 Braunschweig, Germany — [3]École Polytechnique Fédérale de Lausanne, 1015 Lausanne, Switzerland

Peptides have outstanding intriguing functionalities determined by their self-assembled structures. We have investigated the self-assembly of peptides on surfaces to probe the interaction between specific amino acids at sub-molecular length scales. For these high resolution studies we deposited the peptides under ultrahigh vacuum conditions using an electrospray ion beam deposition source and transferred them in-situ into a low temperature scanning tunneling microscope. Our model systems of synthetic peptides consist of eight amino acids including only Arginine, Proline, and Tryptophan. Our results show, how tiny changes within simple peptide sequences drastically influence the self-assembly pattern due to the high conformational freedom of these molecular systems.

O 87.5 Thu 11:45 MA 004

Characterization and prediction of peptide structures on inorganic surfaces — •Dmitrii Maksimov, Carsten Baldauf, and Mariana Rossi — Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany

Interfacing biological molecules with inorganic materials can give access to new technology that joins the versatile character of the biomolecular world with the robust electronic properties of inorganic materials. Peptides, for example, present a large degree of modularity, chemical versatility and conformational adaptability. However, their high degree of conformational freedom makes it a challenge to be able to predict structural motifs and understand the physics governing them. Here we address the structure-search problem by extending a first-principles genetic algorithm package that works on internal degrees of freedom [1] in order to include the position and orientation of molecules with respect to the surface. We show that energy differences between different conformations of the flexible ArgH^+ amino acid on Cu(111) show significant discrepancies when optimized with a force-field (tailored for peptide-surface interactions [2]) and with dispersion-corrected DFT. We further show that the excess charge of the protonated ArgH^+ is efficiently screened upon adsorption on metallic surfaces and that the Arg amino acid adopts a zwitterionic conformation on Cu(111) which considerably increases the molecular dipole parallel to the surface. [1] A. Supady, et al., JCIM 55, 2338 (2015) [2] F. Emami, et al., Chem. Mat. 26, 2647 (2014).

O 87.6 Thu 12:00 MA 004

Electrospray deposition of structurally complex molecules revealed by atomic force microscopy — •Antoine Hinaut[1], Tobias Meier[1], Remy Pawlak[1], Sara Freund[1], Klaus Müllen[2], Silvio Decurtins[3], Thilo Glatzel[1], Akimitsu Narita[2], Shi-Xia Liu[3], and Ernst Meyer[1] — [1]Dep. of Physics, Univ. of Basel, Switzerland. — [2]MPI for Polymer Research, Mainz, Germany — [3]Dep. of Chemistry and Biochemistry, Univ. of Bern, Switzerland

Increasing complexity and functionalization of molecular species studied in ultra high vacuum is actually mainly limited by the deposition technique. We used our electrospray deposition setup[1,2], to introduce two molecular species in ultra high vacuum. The first molecule, based on large aromatic core, includes six long alkyl chains. Assemblies on the Au(111) surface both at room temperature with ncAFM and at low temperature with AFM/STM are observed. Their formation is directed by alkyl-alkyl interaction and is also influenced by the measurement temperature. The second species is a fused electron donor-acceptor molecule. Measurement on the Au(111) surface at low temperature AFM/STM shows small island formation directed by H-bond interaction. In both cases we reach cleanliness levels compatible with high-resolution CO functionalized tip AFM measurements and show the intact chemical structures after electrospray deposition. Therefore our setup combined with high resolution scanning probe measurements allows investigation of more complex compounds with attractive properties. [1] Hinaut et al., BJNano, 2015, 6, 1927-1934. [2] Hinaut et al., submitted to Nanoscale.

O 87.7 Thu 12:15 MA 004

STM studies of functional platform adlayers on Au(111) surfaces — •Talina Rusch[1], Roland Löw[2], Alexander Schlimm[3], Felix Tuczek[3], Rainer Herges[2], and Olaf M. Magnussen[1] — [1]Institute of Experimental and Applied Physics, Kiel University, Germany — [2]Otto Diels Institute of Organic Chemistry, Kiel University — [3]Institute of Inorganic Chemistry, Kiel University

The functionalization of surfaces by self-assembled monolayers is of great interest in nanoscience. We have introduced the so called platform approach, where molecular platforms of Triazatriangulenium (TATA) [1, 2, 3] ions are employed for attaching freestanding functional units to metal surfaces. These platforms provide a well-defined lateral and vertical molecular architecture and the steric demand is controlled by different alkyl side chains. Here, detailed STM studies on different adsorbate layers of TATA derivatives are presented. Specifically, we will discuss the structure of mixed adlayers consisting of two different TATA derivatives, one where the attached azobenzene is fully conjugated and one where it is isolated. We found that those TATA derivatives are perfectly mixable and randomly distributed on the Au(111) surface. Furthermore, we will present direct STM observations of the photoswitching in new azobenzene functionalized TATA adsorbate layers.This work was supported by the Deutsche Forschungsgemeinschaft via SFB 677 "Function by switching". [1] B. Baisch et al., J. Am. Chem. Soc. 131 (2009) 442 - 443. [2] S. Kuhn et al., Phys. Chem. Chem. Phys. 12 (2010) 4481 - 4487. [3] J. Kubitschke et al., Eur. J. Org. Chem. 2010 (2010) 5041 - 5055.

O 87.8 Thu 12:30 MA 004

Supramolecular nanopatterns of arylene-alkynylenes on HOPG: Insights from STM — •Stefan-S. Jester — Universität Bonn, Kekulé-Institut für Organische Chemie und Biochemie, Gerhard-Domagk-Str. 1, 53121 Bonn, Germany.

Arylene-alkynylenes with sufficiently long alkyl/alkoxy side chains form self-assembled monolayers at the solid/liquid interface on graphite (HOPG). 2D crystal engineering relates the size and shape of the molecules with the lattice constants and symmetries of these supramolecular nanopatterns. Scanning tunneling microscopy provides a submolecularly resolved insight. Tesselation concepts can be applied to design cocrystals (e.g., of triangles and hexagons), and the symmetry mismatch between molecule and the substrate lattice leads to complex superstructures (e.g., observed for pentagons).[1] The hierarchical formation of frustrated superstructures is observed for C_{3v} symmetric molecules, but still difficult to predict.[2] Thereby, not only the number of alkoxy side chains per molecule, but also the substitution pattern is crucial for the periodic pattern formation, as we show for molecular spoked wheels.[3] [1] S.-S. Jester, E. Sigmund, S. Höger *J. Am. Chem. Soc.* **2011**, *133*, 11062; [2] S.-S. Jester, E. Sigmund, L. Röck, S. Höger *Angew. Chem. Int. Ed.* **2012**, *51*, 8555; [3] A. Idelson, C. Sterzenbach, S.-S. Jester, C. Tschierske, U. Baumeister, S. Höger *J. Am. Chem. Soc.* **2017**, *139*, 4429.

O 87.9 Thu 12:45 MA 004

Two switchable rotaxanes operating in multilayers on solid support investigated by XPS and NEXAFS — •Thomas Heinrich[1,2], Henrik Hupatz[2], Andreas Lippitz[1], Christoph A. Schalley[2], and Wolfgang E. S. Unger[1] — [1]Bundesanstalt für Materialforschung und -prüfung (BAM), 6.1 Surface Analysis and Interfacial Chemistry, Unter den Eichen 44-46, 12205 Berlin — [2]Institut für Chemie und Biochemie, Freie Universität Berlin, Takustraße 3, 14195 Berlin, Germany

Interfaces provide the structural basis for function as, for example, encountered in nature in the membrane-embedded photosystem or in technology in solar cells. Synthetic functional multilayers of molecules cooperating in a coupled manner can be fabricated on surfaces through layer-by-layer self-assembly. Ordered arrays of stimuli-responsive rotaxanes undergoing well-controlled axle shuttling are excellent candidates for coupled mechanical motion. The present work demonstrates the successful deposition of ordered mono- and multilayers of chemically and photochemically switchable rotaxanes on gold surfaces. Two substrates are investigated - silicon and gold. Of these materials, only gold showed to be suitable for the development of highly preferential oriented rotaxane layers. XPS indicates for both substrates that our layer-by-layer approach worked and a layer growth with every deposition step is present. NEXAFS showed that both stimuli cause an increase of the multilayer's preferential orientation and that the switching is reversible. However, these effects are only observed for the multilayers on gold surfaces.