

O 99: Organic Molecules on Inorganic Substrates VI: Adsorption, Growth and Networks

Time: Thursday 10:30–13:30

Location: GER 38

O 99.1 Thu 10:30 GER 38

Electric Field/ Light-Induced Switching of Spiropyran Derivative on Graphite — ●HIMANI MALIK¹, THOMAS HALBRITTER², ALEXANDER HECKEL², and THIRUVANCHERIL G. GOPAKUMAR¹ — ¹Department of Chemistry, Indian Institute of Technology Kanpur, Kanpur-208016, India — ²Institute for organic chemistry and chemical biology, Goethe-University Frankfurt, Germany

Spiropyran (SP) and its derivatives are known for their switching ability by UV light. SP (closed form), shows reversible ring openings by cleavage of C-O bond and converted into merocyanine (MC, open form). The open form is planar, conjugated and possesses a large dipole moment due to the stabilization of a zwitterion form [1]. The closed and the open forms are distinguished on Au(111) surface as reported before [2]. In the current work, we discuss the self-assembly of SP derivative with a carboxylic group attached to the indoline ring. The carboxylic group offers strong hydrogen bonding interaction, which facilitates the formation of ordered patterns. We show the electrical field and light-induced switching of an adlayer of SP derivative. The SP films are prepared from the solution phase on highly oriented pyrolytic graphite. The microscopic structure and electronic properties are measured using scanning tunnelling microscopy and atomic force microscopy.

1.G. Cottone, et al., Chem. Phys. Lett 2004, 388, 218-222 2.C. Bronner, et al., J. Phys.: Condens. Matter 2011, 23, 484005-12

O 99.2 Thu 10:45 GER 38

Electron transmission through alpha-helical polyalanine investigated by STM and STS — ●NGUYEN THI NGOC HA¹, DIANA SLAWIG², YOSSI PALTIE³, and CHRISTOPH TEGENKAMP^{1,2} — ¹TU Chemnitz, Germany — ²Leibniz University, Hannover, Germany — ³Department of Applied Physics, Hebrew University of Jerusalem, Israel

Alpha-helical molecules recently have attracted much attention in view of electron propagation along the helical backbone structure which comes along with an efficient spin polarization [1]. In this study, we investigated the growth and electronic levels of molecular monolayer structures of helical polyalanine-based peptides (PA) on Au(111) and HOPG surfaces by scanning tunneling microscopy (STM), spectroscopy (STS) under ambient conditions. The self-assembled monolayer (SAM) films revealed a high degree of lateral and rotational order [2]. Due to formation of Au-S bonds on Au(111), resulting from the termination of the helix by cysteine, the PA molecules are oriented and their intrinsic dipole moment is tilted with respect to the surface normal, contrary to HOPG. This charge ordering within the SAM facilitates internal electric fields, which obviously renormalize the molecular orbital energies along the helix, thus enabling a high conductance through these peptides. [1] K. Kitagawa et al., Journal of Polymer Science Part A: Polymer Chemistry 41, 3493, (2003). [2] Nguyen T.N.Ha et al. The Journal of Physical Chemistry C 123, 612, (2019).

Invited Talk

O 99.3 Thu 11:00 GER 38

Exploration of complex interfacial networks and 2D tessellations — ●JOHANNES V BARTH — Physics Department E20, TU Munich - www.e20.ph.tum.de

A major objective in modern surface and nanoscale science relates to complex interfaces and the development of protocols for their control, both in the static and dynamic regime. Interfacial molecular engineering employing optimized assembly procedures and carefully selected molecular tectons represents a powerful tool for constructing a variety of intriguing materials. Herein we report advances towards surface-confined complex networks using different fabrication schemes. Specifically, we realized networks and tessellations via (i) supramolecular organization of organic tectons, (ii) metal-directed assembly, notably exploiting rare-earth centers, (iii) flexible molecular units, and (iv) multi-step convergent synthesis where sequential chemical conversions of a simple organic species mediate the expression of a semiregular archimedean tiling. Our approach illustrates novel avenues to construct complex materials via specific interactions and interfacial adaptation or transformations of adsorbed molecular species. Moreover, the findings and employed methodology contributes to the general understanding of the emergence of complexity and hierarchic systems

in chemistry and biology.

O 99.4 Thu 11:30 GER 38

Explaining Misleading Surface Diffraction Patterns with DFT and Machine Learning — ●ANDREAS JEINDL¹, JARI DOMKE², MALTE SCHULTE³, FALKO SOJKA², and OLIVER T. HOFMANN¹ — ¹Institute of Solid State Physics, NAWI Graz, Graz University of Technology, Austria — ²Institute of Solid State Physics, Friedrich Schiller University Jena, Germany — ³Experimental Physics 1, TU Dortmund, Germany

The determination of the structure of organic thin films and monolayers on inorganic substrates commonly relies on surface diffraction methods, such as LEED. Although the spectra obtained by these methods contain all the necessary information (except the phase) required to directly reconstruct the atomistic structure, in practice the interpretation is far from straightforward. In cases when multiple different models satisfactorily explain the experiment, good scientific practice suggests applying occam's razor and selecting the simplest structure possible.

Here, we highlight several instances where diffraction pattern misleadingly suggest too simple structures due to the presence of orientational domains, disorder, or small structure factors. Using caffeine on Au(111) and acenequinones on Ag(111) as examples, we perform a comprehensive first-principles structure search to independently determine the correct geometry, which is often complex. We discuss the difficulties and interpretation possibilities when trying to compare LEED-data of organic monolayers with theoretically predicted structures for different organic/inorganic interfaces.

O 99.5 Thu 11:45 GER 38

On-surface synthesis of triazine-based porous nanoribbons — ●MIRUNALINI DEVARAJULU, MARTIN HALLER, MIN-KEN LI, SHADI SORAYYA, and SABINE MAIER — Department of Physics, Friedrich-Alexander-Universität Erlangen-Nürnberg, Erlangen, Germany

Covalent triazine frameworks are 2D materials that provide a high chemical stability and plenty of nitrogen sites, which are important for host-guest chemistry and applications as membranes and energy storage materials. Here, we present a low-temperature scanning tunneling microscopy study on the on-surface synthesis of triazine-based porous carbon nanoribbons on Ag(111) using 1,3,5-tris(3-bromophenyl)triazine as a precursor. We followed a thermally induced sequential synthesis based on an Ullmann-type reaction to covalently couple the molecules and a preprogrammed isomerization combined with a dehydrogenation reaction to fabricate the ribbons, as previously reported for all-carbon porous nanoribbons.[1,2] Despite the structural similarity of the precursors, the triazine-based molecules lacked a strong conformational selectivity in the first reaction step, which prevented the ribbon formation. We demonstrate that this can be successfully resolved by following either a bimolecular or a kinetically controlled synthesis, respectively. Finally, we will show that the triazine-based porous nanoribbons are suitable for host-guest experiments using single metal atoms.

[1] M. Ammon, T. Sander, S. Maier, JACS, 2017, 139 (37), 12976.

[2] M. Ammon, et al., ChemPhysChem 2019, 20, 2333.

O 99.6 Thu 12:00 GER 38

Controlling molecular cluster formation by molecule-surface interaction — ●OLE BUNJES¹, LUCAS A. PAUL², TOBIAS CLAUS¹, EMMANOUIL STAVROULAKIS¹, INKE STEWERT², and MARTIN WENDEROTH¹ — ¹IV. Physical Institute, University of Göttingen, Germany — ²Institute of Inorganic Chemistry, University of Göttingen, Germany

Deposition of self-assembling molecules on a surface is a promising approach to control the growth of large scale structures with nanometer precision, as it is necessary in the context of molecular electronics. We use scanning tunneling microscopy (STM) to study the self-assembly of molecular clusters. Sub-monolayer films of the thermally stable complex *fac*-Re(bpy)CO₃Cl (bpy = 2,2'-bipyridine) were deposited on a clean Ag(100) surface at 300 K, and investigated by STM at low temperatures. The initial steps of cluster formation are found to strongly depend on the presence of step edges with a specific geometric orientation. Attached molecules affect Ag atom diffusion so that the

neighboring step segments preferentially align along the same direction, thereby increasing the probability for further molecules to attach to the clusters. This molecule-surface interaction is found to play a major role for the growth of *fac*-Re(bpy)CO₃Cl-structures of different dimensions, e.g., for chain and monolayer growth. We acknowledge the financial support by the DFG via the SFB 1073 (projects C4 and C1).

O 99.7 Thu 12:15 GER 38

Electrospray Controlled Ion Beam Deposition as a powerful tool to deposit biomolecules on a solid support under UHV with subsequent STM imaging — ●KAROLINA STOIBER, ANDREAS WALZ, PETER KNECHT, ANTHOULA PAPAGEORGIOU, JOACHIM REICHERT, ANNETTE HUETTIG, HARTMUT SCHLICHTING, and JOHANNES V. BARTH — Physics E20, Technical University of Munich, Germany

Biomolecules gain interest in surface science and nanotechnology as potential building blocks in nano-sized structures or new materials. Their thermal fragility and lack of sublimation capacity make them ineligible for classical deposition technologies such as OMBE. Our new preparative approach based on electrospray ionization with controlled ion beam deposition (ES-CIBD) unlocks this potential. Data obtained with plasmid DNA, insulin and spermine are presented, representing three chemical classes (nucleic acids, proteins, polyamines) and molecular masses from 200 Da to 2 MDa. We applied negative and positive spray modes and tested different conformations introduced by variation of pH, ionic strength or by enzymatic manipulation. The ionization principle described by the charge residue model and chain ejection model is primarily determined by the outer shape of the molecule: here we experimentally compare globular and elongated forms. Parameters to evaluate the preparation process and quality of deposition are mass spectra to assess selectivity, ion currents for efficiency and imaging the deponents on Ag(111) and Cu(111) by UHV-STM for integrity. In conclusion, ES-CIBD is a versatile tool to selectively and efficiently deposit biomolecules on solid supports while the structure is preserved.

O 99.8 Thu 12:30 GER 38

Molecule-Surface Collision Explores the Chemical and Conformation Space of a Molecule — ●KELVIN ANGGARA — Max Planck Institute for Solid State Research, Stuttgart

Molecule-surface collision is fundamental in wide array of contemporary topics, ranging from material science to structural biology. From scattering experiments at gas-surface interface, much of the collision dynamics is known for diatomic molecules colliding with a surface - but not for polyatomics. Here, we study the dynamics of polyatomic-surface collision in vacuo by combining electrospray ionization and single-molecule microscopy. Using the electrospray ion-beam deposition (ES-IBD) technique, a beam of polyatomic ions was aimed normal to a metal surface with a known translational energy. The resulting collision outcome was imaged using Scanning Tunneling Microscopy (STM) to allow inference of the collision dynamics. The key finding here is that, upon collision, the molecular translation is converted to low-frequency molecular vibrations, which consequently trigger: (i) a chemical reaction at 5 - 50 eV collision energy; or (ii) a conformation change at 0.5 - 5 eV. The former is exemplified by a Reichardt Dye colliding with a Cu(100) surface that gave a bond-selective reaction via mechanical compression of the whole molecule; While, the latter is exemplified by a Cellohexaose colliding with Cu(100) that resulted in an exploration of the conformation space, i.e. folding motifs, of the oligosaccharide. The general approach described here thus allows the use of molecule-surface collision as a means to explore different regions of potential energy surface for any molecule that can be electrosprayed.

O 99.9 Thu 12:45 GER 38

Global approach to prediction and modeling of biomolecules on surfaces — ●JOHANN CHRISTIAN SCHÖN¹, JUAN CORTES², NATHALIE TARRAT³, BOHDAN ANDRIYEVSKY⁴, SABINE ABB¹, STEPHAN RAUSCHENBACH⁵, and KLAUS KERN^{1,6} — ¹MPI FKF, Stuttgart, Germany — ²LAAS-CNRS, Toulouse, France — ³CEMES-CNRS, Toulouse, France — ⁴TU Koszalin, Koszalin, Poland — ⁵Dept.

Chemistry, University Oxford, Oxford, UK — ⁶EPFL, Lausanne, Switzerland

Biomolecules on surfaces exhibit a large variety of individual conformations and self-assembly patterns, whose prediction is a great challenge. We have developed a systematic global energy landscape based approach to generate models for individual molecules and their assemblies[1]. Individual molecules are globally optimized in the gas phase, and the optimal configurations are placed on the substrate for a second global search using a rapidly-growing random-tree based algorithm, followed by an ab initio relaxation and energy ranking. Finally, the best conformations are used as building blocks for models of the assembly and / or as input conformations for global optimizations of multi-molecule patterns; the resulting multi-molecule assemblies can then be compared with experimental data. We demonstrate this approach at the example of two disaccharides, trehalose[2] and sucrose[3], that had been deposited on a Cu-100 surface and imaged via STM.

[1] J. C. Schön et al., Z. Naturf. B, 2016, 71:351-374 [2] S. Abb et al., RSC Advances, 2019, 9:35813-35819 [3] S. Abb et al., Angew. Chemie, 2019, 131:8424-8428

O 99.10 Thu 13:00 GER 38

Growth of N-heterocyclic carbenes on a deactivated semiconductor surface — ●MARTIN FRANZ¹, SANDHYA CHANDOLA², MAXIMILIAN KOY³, ROBERT ZIELINSKI², MATTHIAS FREITAG³, CONOR HOGAN⁴, FRANK GLORIUS³, NORBERT ESSER², and MARIO DÄHNE¹ — ¹Institut für Festkörperphysik, Technische Universität Berlin, D-10623 Berlin, Germany — ²Leibniz-Institut für Analytische Wissenschaften - ISAS e.V., 12489 Berlin, Germany — ³Organisch-Chemisches Institut, Westfälische Wilhelms-Universität Münster, D-48149 Münster, Germany — ⁴Istituto di Struttura della Materia-CNR (ISM-CNR), 00133 Rome, Italy

Self-assembled monolayers based on N-heterocyclic carbenes (NHCs) are promising for surface functionalization as ultra-stable alternatives to thiol based systems. Here, we report on the ordered growth of NHCs on silicon, demonstrating the versatility of NHCs as anchors for surface functionalization. In a detailed scanning tunneling microscopy and first principles calculations study, we investigate the adsorption of the prototypical NHC 1,3-bis(dimethyl)imidazolium (IME) on the deactivated Si(111) $\sqrt{3} \times \sqrt{3}$ R30°-B surface. We find a vertical adsorption geometry of the molecules above the Si adatoms of the substrate. At low IME coverage, a rotation of the molecules leads to a round appearance in the STM images, while at high NHC coverages an ordering of the molecules into a $2\sqrt{3} \times \sqrt{3}$ R30° superstructure is observed.

O 99.11 Thu 13:15 GER 38

Gas adsorption on hydrophobic surfaces near the critical point — ●MIKE MORON, GÖRAN SURMEIER, MARC MORON, JENNIFER BOLLE, JULIA NASE, MICHAEL PAULUS, and METIN TOLAN — Fakultät Physik/DELTA, TU Dortmund, 44227 Dortmund, Germany

Hydrophobic surfaces and their interaction with their environment are of great importance in current research. One important example is the interaction between the so-called surfactants in the alveoli of the lung and the surrounding gas. The surfactants form monolayers inside the alveoli, that are orientated with their hydrophobic hydrocarbon chains towards the gas space. Together with various proteins, the surfactants are involved in the gas exchange and the stabilization of the alveoli. Since the surfactant monolayers are in direct contact with the inhaled air, including argon and CO₂, it is essential to investigate the interaction in order to understand the processes involved. Another important example is the adsorption of CO₂. The usage of metal-organic frameworks (MOFs) appear to be a promising method for storing CO₂. A self-assembled octadecyltrichlorosilane (OTS) monolayer on a silicon wafer, served as hydrophobic surface. The gases under investigation were CO₂ and Ar at different gas pressures. Besides, we used hexafluorethane (C₂F₆) to study the effect of different gases on the adsorption behavior. We performed an X-ray-reflectivity experiment with a beam energy of 27 keV at the beamline BL9 at DELTA, allowing to resolve the formed structures and gas adsorption layers.