O 64: Focus Session: Molecular Nanostructures on surfaces - New Concepts towards Complex Architectures IV

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

(Synopsis provided with part I of this session)

Time: Wednesday 15:00–18:15 Location: MA 004

O 64.1 Wed 15:00 MA 004

Crystallization of a Two-Dimensional Hydrogen-Bonded Molecular Assembly: Evolution of the Local Structure Resolved by Atomic Force Microscopy — •Laerte L. Patera[1], Xunshan Liu[2], Nico Mosso[3], Silvio Decurtins[2], Shi-Xia Liu[2], and Jascha Repp[1] — [1]University of Regensburg, Regensburg, Germany — [2]University of Bern, Bern, Switzerland — [3]IBM Research-Zurich, Rüschlikon, Switzerland

Noncontact Atomic Force Microscopy (nc-AFM) provides detailed insights into the structure of surface-supported molecular self-assemblies, overcoming restrictions given by scanning tunneling microscopy (STM). Here we resolved the structures of the aromatic N-heterocyclic hexaaza-triphenylene (HAT) molecular synthon with sub-Å resolution by means of nc-AFM, both in the kinetically trapped amorphous state and in the thermo-dynamically stable crystalline phase. These results reveal how the crystallization governs the length scale of the network order for non-flexible molecular species without affecting the local bonding schemes. The capability of nc-AFM to accurately resolve structural relaxations will be highly relevant for the characterization of vitreous two-dimensional supramolecular materials.

O 64.2 Wed 15:15 MA 004

Assigning the absolute configuration of chiral aliphatic compounds by direct visual inspection of individual molecules — Daniel Ebeling[1], Marina Sekutor[2], Marvin Stiefermann[1], Jalmar Tschakert[1], Jeremy Dahl[3], Robert Carlson[3], Peter Schreiner[2], and •Andre Schirmeisen[1] — [1]Institute of Applied Physics, Justus-Liebig University Giessen, Germany — [2]Institute of Organic Chemistry, Justus-Liebig University Giessen, Germany — [3]cStanford Institute for Materials and Energy Sciences, Stanford, USA

Deciphering the absolute configuration of a single molecule by direct visual inspection is the next step in direct compound identification, with far-reaching implications for medicinal chemistry, pharmacology, and natural product synthesis. Here we demonstrate the feasibility of this approach utilizing low temperature atomic force microscopy (AFM) with a CO-functionalized tip to determine the absolute configuration and orientation of single adsorbed [123]tetramantane molecule, the smallest chiral diamondoid. We differentiate between single enantiomers on a Cu(111) surface by direct visual inspection with atomic precision, and furthermore identify molecular dimers and small molecular clusters. The experimental results were also confirmed by a computational study that additionally allowed quantification of the corresponding intermolecular interactions. The unique toolset of absolute configuration determination combined with AFM tip manipulation now opens the route for unprecedented molecular nucleation studies, including chirality driven assembly or reaction mechanisms.

O 64.3 Wed 15:30 MA 004

Surface induced asymmetric activation of 4,4”-Diamino-p-terphenyl on Cu(111): symmetry breakdown by lattice mismatch — Qigang Zhong[1], •Daniel Ebeling[2], Jalmar Tschakert[2], Yixuan Gao[3], Deliang Bao[3], Shixuan Du[3], Lifeng Chi[1], and Andre Schirmeisen[2] — [1]Institute of Functional Nano & Soft Materials, Soochow University, Suzhou, China — [2]Institute of Applied Physics, Justus-Liebig University, Giessen, Germany — [3]Institute of Physics, Chinese Academy of Sciences, Beijing, China

We demonstrate that asymmetric activation of the mirror symmetric molecule 4,4”-Diamino-p-terphenyl (DATP) is possible on a metal surface. Our low temperature atomic force microscopy images, using CO-tip functionalization, show that on Cu(111) the DATP the adsorption geometry becomes asymmetric for certain orientations, while on Au(111) the symmetry is fully retained. This symmetry breaking on Cu(111) is caused by a lattice mismatch between the molecule and the metal surface, corroborated by interactions with the subsurface atomic layer. The asymmetric DATP molecules show non-stationary behavior under the influence of the scanning tip, which leads to a bi-level telegraph noise, here serving as a fingerprint of the surface induced asymmetry. Dispersion corrected DFT-D2 computations confirm the precise topology, the dynamics, and the energy barriers of the observed asymmetric adsorption geometries. Finally, we exploit the asymmetric activation of DATP for side-preferential attachment of 2-triphenylenecarbaldehyde (TPCA). Our findings provide a new route for surface induced asymmetric activation of a symmetric compound.

O 64.4 Wed 15:45 MA 004

Interaction of molecules with doped graphene via noncovalent interactions — •Bruno de la Torre[1,2], Martin Svec[1,2], Rabindranath Lo[3], Pavel Jelinek[1,2], Radek Zboril[2], and Pavel Hobza[2,3] — [1]Regional Centre of Advanced Technologies and Materials, Palacký University, Olomouc, Czech Republic. — [2]Institute of Physics of the CAS, Prague, Czech Republic. — [3]Institute of Organic Chemistry and Biochemistry of the CAS, Prague, Czech Republic.

Chemical doping of graphene is an efficient way of tuning its intrinsic properties. In particular, implantation of a single-atom dopant [1,2] modifies graphene local electronic structure and consequently its chemical activity [3]. Understanding the interaction of molecules with individual dopants in graphene is of immense importance for development of graphene-based devices. We study the interaction of iron(II) phthalocyanine (FePc) with both pristine and N-doped graphene by means of cryogenic STM+AFM. While on pristine graphene the FePc forms regularly ordered self-assemblies, the presence of nitrogen dopants anchors FePc non-covalently, preventing their long-range ordering (see Fig.1). By STS and manipulation with the molecules we investigate how the proximity of the N-dopant affects the electronic states of a FePC molecule. The AFM high-resolution imaging with a CO-tip reveals a substantial charge redistribution within the molecule.

[1] M. Telychko et al. ACS Nano 8 (7), 7318 (2014), [2] A. Martin-Recio et al. Nanoscale 8, 17686 (2016) [3] M. Telychko et al. ACS Nano 9 (9), 9180 (2015)

O 64.5 Wed 16:00 MA 004

Resolving molecular products of surface induced chemical reactions of 9-Azidophenanthrene — •Aleš Cahlík[1], John Hellerstedt[1], Pingo Mutombo[1], Oleksander Stetsovych[1], Ivo Starý[2], Irena Stará[2], Martin Švec[1], and Pavel Jelínek[1] — [1]Institute of Physics, Czech Academy of Sciences, Praha, Czech Republic — [2]Institute of Chemistry and Biochemistry, Czech Academy of Sciences, Praha, Czech Republic

The preparation of suitable systems for controllable, light-driven molecular switches presently remains an appealing experimental challenge. Recently, azo-compounds have proven to be an auspicious choice for such purpose. We report the on-surface synthesis and identification of azo-phenanthrene isomers, a prospective molecular switch, using azide-based 9-Azidophenanthrene (APT) as a molecular precursor. Due to the high reactivity of APT, a broad variety of reaction pathways exist which results in an extensive mixture of products. Such chemical diversity is hard to grasp by means of a conventional chemical analysis tools owing to the subtle structural differences with nearly identical bond environments. In our experiment, we went beyond the limits of these techniques by employing non-contact atomic force microscopy to achieve submolecular resolution of the product species. We speculate that the precursor decomposes into highly reactive nitrene species, that subsequently form a diverse mixture of products. By close comparison with theoretical calculations we are able to distinguish between covalently (N=N) bonded azo-phenanthrene isomers and other non-covalently bonded molecular structures.

O 64.6 Wed 16:15 MA 004

On-surface synthesis of nitrogen-doped 5-7-membered nanographenes — •Frank Eisenhut[1,2], Dmitry Skidin[1,2], Justus Krüger[1,2], Marcus Richter[1,3], Reinhard Berger[1,3], Xinliang Feng[1,3], Francesca Moresco[1,2], and Gianaurelio Cuniberti[1,2,4] — [1]Center for Advancing Electronics Dresden (cfaed), TU Dresden, 01062 Dresden, Germany — [2]Institute for Materials Science, TU Dresden, 01069 Dresden, Germany — [3]Institute for Molecular Functional Materials, TU Dresden, 01062 Dresden, Germany — [4]Dresden Center for Computational Materials Science (DCMS), TU Dresden, 01069 Dresden, Germany

We present the on-surface synthesis of five- and seven-membered nitrogen-doped "defective" nanographene molecules by thermally induced cyclodehydrogenation of a nitrogen-containing polycyclic hydrocarbon on the Au(111) surface. The reaction is investigated by scanning tunneling microscopy (STM) at low-temperature. After annealing, we observe mainly non-symmetric planar products. High-resolution STM images on single molecules show the formation of a five- and a seven-membered ring, while the planarity is obtained by the cleavage of one phenyl-group. In a few cases, we observe non-planar bowl-shaped molecules with an Azacorannulene core. This indicates the complete conversion of the precursor molecule into a nitrogen-doped nanographene with four odd-numbered rings. Using scanning tunneling spectroscopy, we investigate the electronic structure of all molecular species.

15 min. break

O 64.7 Wed 16:45 MA 004

The role of tip reactivity in intramolecular imaging of organic molecules in NC-AFM — •Adam Sweetman[1], Sam Jarvis[2], Philipp Rahe[3], and Philip Moriarty[1] — [1]School of Physics and Astronomy, University of Nottingham, U.K. — [2]School of Physics, University of Lancaster, UK — [3]Department of Physics, University of Osnabrück, Germany

Noncontact atomic force microscopy (NC-AFM) is now routinely capable of obtaining submolecular resolution, readily resolving the carbon backbone structure of planar organic molecules adsorbed on metal substrates. However, normally this resolution requires functionalisation of a metal tip by a carbon monoxide (CO) molecule or similar passivating group.

In this work, we show that the same resolution may also be obtained for molecules adsorbed on a reactive semiconducting substrate, and that surprisingly, this resolution is routinely obtained without the need for deliberate tip functionalization [1].

Counter to intuitive expectations, we find that many silicon terminated tips do not react strongly with the adsorbed organic molecules, and we find that only specific highly oriented clusters have sufficient reactivity to break open the existing carbon-carbon bonds [2]. Our results suggest a wide range of tips may be capable of producing intramolecular contrast for molecules adsorbed on semiconductor surfaces.

1. Sweetman, A. et al. Phys. Rev. B 94, 115440 (2016).
2. Sweetman, A. et al. Phys. Rev. B 90, 165425 (2014).

O 64.8 Wed 17:00 MA 004

Probing intermolecular interactions in a molecular layer via single-molecule manipulation — •Christian Wagner[1,2], Philipp Leinen[1,2], Alexander Diener[1,2], Ruslan Temirov[1,2], and F. Stefan Tautz[1,2] — [1]Peter Grünberg Institut (PGI-3), Forschungszentrum Jülich, Germany — [2]Jülich Aachen Research Alliance (JARA)-Fundamentals of Future Information Technology, Jülich, Germany

Adsorption of large organic molecules is often influenced by their functional groups which may simultaneously interact with the surface and neighboring molecules. Together with the mechanical flexibility of molecules this leads to a multidimensional, highly structured and typically rather shallow interaction potential landscape which can hardly be investigated by any other means than theoretical simulations. Here we show that non-contact atomic force microscopy (NC-AFM) facilitates single-molecule manipulation protocols which enable probing the potential energy surface in a molecular layer. We apply the manipulation to the archetypal model system PTCDA (perylene-3,4,9,10-tetracarboxylic dianhydride) on Ag(111) and study the influence of polar groups, specifically of weak hydrogen bonds on the intermolecular potential. Fitting a force-field model to our experimental data reveals how electrostatic interactions cause out-of-plane forces on partially charged atoms. Our results intuitively explain how such interactions can alter the vertical adsorption geometry of a molecule in a layer compared to an isolated molecule.

O 64.9 Wed 17:15 MA 004

Mechanical response while pulling a single poly-pyrene chain on gold — •Rémy Pawlak[1], Philipp D'Astolfo[1], Guilherme Vilenha[2], Tobias Meier[1], Thilo Glatzel[1], Shi-Xia Liu[3], Silvio Decurtin[3], Ruben Perez[2], and Ernst Meyer[1] — [1]Physics Department,University of Basel, Switzerland — [2]Departamento de Fisica Teorica de la Materia Condensada, Universidad Autonoma de Madrid, Spain — [3]Department of Chemistry and Biochemistry, University of Berne, Switzerland

The intamolecular mechanics of a molecule govern its diffusion while sliding over a surface. Quantifying such aspect at the molecule level is however challenging and poorly observed so far [1-3]. Here, we synthesized long polypyrene chains linked by C-C bonds on Au(111) and proceed to their vertical and lateral manipulations with the apex of an atomic force microscope. Combined force measurements and numerical calculations show that periodic modulations in the force response arise from the detachment of single pyrene units from the surface as well as their sliding over the surface lattice potential. These periodicities show that the remaining pyrene on the surface ”snake” during manipulations to adapt its commensurability with the surface lattice as well as reduce the mechanical stress induced by the lifted units. [1] Kawai et al. Proc. Natl. Acad. Sci. USA 2014, 111, 3968-3972. [2] Kawai et al. Science 2016, 351, 957-961. [3] Pawlak et al. ACS Nano 2016 10, 713-722

O 64.10 Wed 17:30 MA 004

Single molecule manipulation via inelastic electron tunneling — •Gitika Srivastava[1], Tibor Kudernac[2], Manfred Parschau[1], Peter Stacko[3], Bernard L. Feringa[3], and Karl-Heinz Ernst[1,4] — [1]Empa, Swiss Federal Laboratories for Materials Science and Technology, Dübendorf, Switzerland — [2]University of Twente, The Netherlands — [3]Univeristy of Groningen, The Netherlands — [4]University of Zürich, Switzerland

Maneuvering individual molecules over a clean and unmodified surface is challenging, yet possible using surface sensitive techniques like Scanning Tunneling Microscopy (STM). Electronic and vibrational excitation by means of inelastic electron tunneling from the tip of STM has been observed to have brought out subsequent dynamical processes on surfaces. We investigate the influence of inelastic electron tunneling on molecules with two functional unidirectional rotor units, comparable to the previously reported 4-wheeler as nano-car and have observed molecular motions like hopping and conformational changes. Results of single molecular dynamics of these molecules at low temperatures (6K) on Cu(111) surface are presented and discussed.

O 64.11 Wed 17:45 MA 004

Controlled dissociation of intramolecular bonds by STM manipulation — •Donato Civita[1], Stefan Hecht[2], and Leonhard Grill[1] — [1]Department of Physical Chemistry, University of Graz, Austria — [2]Institute of Chemistry, Humboldt-Universität zu Berlin, Germany

Manipulation of molecules adsorbed at surfaces is very appealing to control and understand fundamental chemical processes. Chemical reactions can be triggered in single molecules by using the energy of the tunneling electrons in a scanning tunneling microscope (STM). Specifically, chemical bonds within molecules can be cleaved [1], the resulting fragments can be pulled across the surface by lateral manipulation with the STM tip and even new bonds can be formed [2].

In this work, we study the dissociation of single Br atoms from dibromoterfluorene (DBTF) molecules adsorbed on the Ag(111) surface. Experiments were done with a low temperature STM and applying voltage pulses where the Br substituents are located. By studying the current signal during the voltage pulse as well as imaging the single molecule before and after such a manipulation, we obtain insight into the process. After dissociation, single Br atoms and the remaining molecule are laterally dislocated over the surface, which reveals details about the interatomic interactions.

[1] B. C. Stipe, M. A. Rezaei, W. Ho, S. Gao, M. Persson, and B. I. Lundqvist, Phys. Rev. Lett. 78, 4410 (1997)

[2] S.-W. Hla, L. Bartels, G. Meyer, and K.-H. Rieder, Phys. Rev. Lett. 85, 2777 (2000)

O 64.12 Wed 18:00 MA 004

Reversible 2D phase transition driven by an electric field: visualization and control on the atomic scale — Ben Wortmann[1], Dennis van Voerden[1], •Paul Graf[1], Roberto Robles[2], Paula Abufager[2], Nicolás Lorente[2], Christian Bobisch[1], and Rolf Möller[1] — [1]Faculty of Physics, Center for Nanointegration Duisburg-Essen, University of Duisburg-Essen, 47048 Duisburg, Germany — [2]ICN2 Catalan Institute of Nanoscience and Nanotechnology,

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We report on a reversible structural phase transition of a two dimensional system which can be locally induced by an external electric field. [1] By means of scanning tunneling microscopy (STM) we determined two coexisting structural configurations of a CO monolayer on Cu(111): an α-phase (7×7 superstructure) and a β-phase ($3\sqrt{3} \times 3\sqrt{3}$) R30°. The balance of the two phases can be shifted by the electric field of the STM tip, causing the domain boundaries to move, increasing the area of the favored phase controllable both in location and size. If the field is further enhanced new domains nucleate. The arrangement of the CO molecules on the Cu surface is observed in real time and real space with atomic resolution while the electric field driving the phase transition is easily varied over a broad range.Our new manipulation mode permits us to bridge the gap between spontaneous long-range ordering of phase transitions and man-made CO structures created by molecular manipulation of CO adlayers.

[1] B. Wortmann et al., Nano Letters **16** (1), 528-533 (2016)