

O 83: Organic Molecules on Inorganic Substrates VI: Chirality, Charge Transfer, Self-Assembly

Time: Thursday 15:00–17:30

Location: H9

O 83.1 Thu 15:00 H9

Supra-molecular spirals formed by self-assembly of spiral shaped molecules — ●JAN VOIGT¹, MILOS BALJOZOVIC¹, KÉVIN MARTIN², NARCIS AVARVARI², KARL-HEINZ ERNST¹, and CHRISTIAN WÄCKERLIN¹ — ¹Empa, Dübendorf, Switzerland — ²Université d'Angers, France

The interdependence of macroscopic and molecular chirality, which is ubiquitous in nature, is still lacking scientific insight. Here, the 2D crystallization of benzene-1,3,5-tris[4]helicene on the Ag(111) surface is studied with scanning tunneling microscopy. The molecules consist of three [4]helicene subunits, which are intrinsically chiral, attached to a central benzene ring via sigma bonds. The helical arms have a low barrier of inversion and the sigma bonds allow for additional configurational flexibility. Indeed, deposition on the sample kept at room temperature leads to self-assembled, homochiral arrays of spiral shaped trishelices. Above a critical coverage, mesoscopic supramolecular spirals are formed. These supramolecular arrangements occur with different topology and their handedness is determined by the chirality of the molecular spirals in the self-assembled domain.

O 83.2 Thu 15:15 H9

Two-dimensional racemate crystallization of trioxa-[11]helicene molecules on Ag(100) surface — ●BAHAAEDDIN IRZIQAT¹, SHYAM SUNDAR², ASHUTOSH BEDEKAR², and KARL-HEINZ ERNST¹ — ¹Empa, Dübendorf, Switzerland — ²University of Baroda, Vadodara, India

Intermolecular chiral recognition in two-dimensional self-assembly on metal surfaces is of paramount importance for enantiomeric separation and heterogeneous enantioselective catalysis for the production of chiral pharmaceuticals and liquid crystal devices. Two-dimensional nucleation and crystallization of a racemic mixture of the helical aromatic hydrocarbon trioxa-[11]helicene (7,12,17-trioxa[11]helicene) on the single crystalline (100) surface of silver has been studied using a combination of scanning tunneling microscopy and theoretical molecular modeling. After deposition on the surface kept at room temperature, the molecules form islands that are comprised of domains in line with the principal directions of the substrate. The domains are heterochiral, with alternating enantiomer sequence in one lattice direction and non-alternating enantiomer sequence in the other.

Invited Talk

O 83.3 Thu 15:30 H9

Control of charge transfer into large organic molecules on ultrathin MgO(001) films — ●MARTIN STERRER — University of Graz, Graz, Austria

Charge transfer processes on ultrathin, supported oxide films have received increasing attention in recent years because of the possibility to control the charge state of adsorbates or the direction of catalytic reactions. The main driving forces for the occurrence of charge transfer in these systems is the reduction of the substrate work function induced by deposition of the oxide film in combination with an adsorbate with high electron affinity. While previous studies have focused on the charging of metal atoms (e.g. Au) or small molecules (e.g. O₂, NO₂), we have recently extended these investigations to charge transfer processes into large organic molecules. In this contribution, we present results on the adsorption and charging of pentacene (5A) and tetraphenylporphyrin (2H-TPP) on ultrathin MgO(001) films supported on Ag(001). By combining scanning tunneling microscopy and photoemission spectroscopy and tomography, we are able to identify and quantify charge transfer into the organic monolayer film. In addition, we show that by variation of the work function and the MgO thickness it is possible to drive the system into a state where no charge transfer occurs. In the case of 2H-TPP charge transfer also appears to strongly influence the self metalation of 2H-TPP to Mg-TPP. Thus, our investigations lay the basis for the ultimate control of charge transfer, and the related chemistry, on ultrathin oxide film systems.

O 83.4 Thu 16:00 H9

Chirality transfer through multistep reaction processes — ●MOHAMMED S. G. MOHAMMED^{1,2}, NESTOR MERINO-DÍEZ^{1,2,3}, JESUS CASTRO-ESTEBAN⁴, JAMES LAWRENCE^{1,2}, ALEJANDRO BERDONCES LAYUNTA^{1,2}, LUCIANO COLAZZO^{1,2}, JOSE IGNACIO PASCUAL^{3,5}, DIEGO PEÑA⁴, and DIMAS G. DE OTEYSA^{1,2,5} —

¹Donostia International Physics Center (DIPC), San Sebastian, Spain — ²Materials Physics Center, Centro de Física de Materiales (CSIC/UPV-EHU), San Sebastian, Spain — ³CIC nanoGUNE, San Sebastián, Spain — ⁴Centro de Investigación en Química Biológica e Materiales Moleculares (CIQUS), Departamento de Química Orgánica, Universidade de Santiago de Compostela, Santiago de Compostela, Spain — ⁵Ikerbasque, Basque Foundation for Science, Bilbao, Spain

Besides its interest for potential optoelectronic devices, molecular chirality is of utmost importance in biology and medicine. Consequently relevant is the selective synthesis of enantiopure molecular compounds, which has been hardly addressed in the growing field of on-surface synthesis. In this frame, 2,2*-dibromo-9,9*-bianthracene reactants are known to form chiral graphene nanoribbons on coinage metal substrates through a complex multi-step reaction including an initial polymerization by Ullmann coupling and following cyclodehydrogenation steps. In this work we show how, starting from enantiopure reactants deposited onto Au(111), their chirality is sequentially transferred to the polymers and finally to the GNRs with an excellent level of selectivity. Unambiguous evidence of this effect is obtained by high-resolution images of the polymers and GNRs at the single molecule level.

O 83.5 Thu 16:15 H9

Influence of Substrates on Self-Assembled Terphenyl Monolayers Investigated by NC-AFM and FM-KPFM — ●NIKLAS BIERE¹, SASCHA KOCH², PATRICK STOHMANN², YANG YANG², ARMIN GÖLZHÄUSER², and DARIO ANSELMETTI¹ — ¹Experimental Biophysics & Applied Nanoscience, University of Bielefeld, Germany — ²Physics of Supramolecular Systems and Surfaces, University of Bielefeld, Germany

Carbon Nano Membranes (CNM) are mechanical stable and homogeneous quasi 2D systems, which are formed by electron radiation induced, cross-linked self-assembled monolayers (SAM). Contrary to graphene, the CNM structural and functional properties can be tailored by the selection of precursors for the SAM formation [1]. CNMs show the capability to act as a molecular sieve to filter e.g. water molecules from impurities with extraordinary efficiency [2]. While this result promises remarkable applications, the actual process of CNM formation as well as their structure and the mechanism for water permeation is still in the focus of our investigations. Furthermore, the choice of substrate influences the self-assembly of our precursor molecules more than previously expected, even with isoelectronic surfaces like gold and silver. In this work, we will present data acquired by noncontact AFM combined with FM-KPFM under ultra-high vacuum conditions to investigate and compare the morphology of in-situ prepared SAMs and CNMs of terphenylthiols on Au(111) and Ag(111).

[1] A. Turchanin, A. Gölzhäuser, *Adv. Mater.* 28 (2016) 6075-6103.
[2] Y. Yang et al., *ACS Nano* 12 (2018) 4695-4701.

O 83.6 Thu 16:30 H9

Large thermal expansion of a self-assembling monolayer in UHV — ●SEBASTIAN SCHERB¹, ANTOINE HINAUT¹, GUILHERME VILHENA¹, RÉMY PAWLAK¹, AKIMITSU NARITA², THILO GLATZEL¹, and ERNST MEYER¹ — ¹Department of Physics, University of Basel, Basel, Switzerland — ²Max Planck Institute for Polymer Research, Mainz, Germany

Self-assemblies of structurally complex molecules in UHV provide interesting prospects for applications in optoelectronics, nanomechanical devices and molecular electronics. To investigate their viability for specific applications, high-resolution studies of their behavior under a variety of conditions are required.

In this study we report the experimental and theoretical study of the adsorption behavior of a molecular assembly on Au(111) under different thermal conditions. A shape persistent polyphenylene Spoked Wheel molecule [1] was deposited onto Au(111) surfaces in UHV by electrospray deposition [2]. The assembly formation studied at room temperature by ncAFM and at low temperature by STM/AFM shows a large positive thermal expansion coefficient from LT to RT. Comparing with molecular dynamics simulations we propose an explanation of the mechanism of expansion due to alkyl chain mobility in combination with increased molecular diffusion.

[1] Liu, Y. et al., *J. Am. Chem. Soc.*, 138, 15539-15542 (2016). [2] Hinaut et al., *Nanoscale*, 10, 1337-1344 (2018).

O 83.7 Thu 16:45 H9

Structure and electronic properties of end states of self-assembled 1D covalent molecular chains on Au(111) — ●ALES CAHLIK¹, JACK HELLERSTEDT¹, MARTIN SVEC¹, VJAI MEENA SANTHINI¹, SIMON PASCAL², PINGO MUTOMBO¹, KAREL VÝBORNY¹, OLIVIER SIRI², and PAVEL JELINEK¹ — ¹Institute of Physics, ASCR, v.v.i., Cukrovarnická 10, CZ-16253 Praha 6, Czech Republic — ²Aix Marseille Université, CNRS, CINaM UMR 7325, 13288, Marseille, France

1D structures offer a rich ecosystem for realizing quantum states with potential application for advanced information technologies. Surface confined molecular self-assembly is one avenue for creating 1d systems, where the extant structure is controlled by the precursor shape, and functional group interlinking chemistry. Here we study self-assembled 1d chains of zwitterionic molecule bis-bidentate ditopic (DABQDI) on Au(111) in ultrahigh vacuum, measured at 5K using combined scanning tunneling and non-contact atomic force microscopies (STM/nc-AFM). Submolecular resolution achieved with a CO-functionalized tip offers detailed structural information, specifically regarding the unusual hydrogen bonds linking the precursor units. In-gap electronic states near the Fermi energy are observed via scanning tunneling spectroscopy (STS), strongly localized to the chain ends. We present our latest efforts to understand and simulate the observed structures via density functional theory (DFT) and nc-AFM simulations, and rationalize the observed electronic properties via modelling inspired by the Su, Schrieffer, Heeger (SSH) one-dimensional tight binding model.

O 83.8 Thu 17:00 H9

Adsorption Structure of Mono- and Diradicals on a Cu(111) Surface: Chemoselective Dehalogenation of 4-Bromo-3'-iodo-p-terphenyl — ●DANIEL EBELING¹, QIGANG ZHONG², TOBIAS SCHLÖDER³, JALMAR TSCHAKERT¹, PASCAL HENKEL³, SEBASTIAN AHLES⁴, LIFENG CHI², DOREEN MOLLENHAUER³, HERMANN A. WEGNER⁴, and ANDRE SCHIRMEISEN¹ — ¹Institute of Applied Physics, Justus Liebig University Giessen, Heinrich-Buff-Ring 16, 35392 Giessen, Germany — ²Institute of Functional Nano & Soft Materials (FUNSOM), Soochow University, 215123 Suzhou, P. R. China — ³Institute of Physical Chemistry, Justus Liebig University Giessen, Heinrich-Buff-Ring 17, 35392 Giessen, Germany — ⁴Institute of Organic Chemistry, Justus Liebig University Giessen, Heinrich-Buff-Ring

17, 35392 Giessen, Germany

For building molecular nanostructures on surfaces the knowledge about the precise adsorption geometry of intermediates at different stages during the reaction process and their interactions with surface atoms or adatoms is of fundamental importance. We show the selective dehalogenation of 4-bromo-3'-iodo-p-terphenyl on Cu(111) using bond imaging atomic force microscopy with CO functionalized tips. The deiodination and debromination reactions are triggered either by heating or locally applying voltage pulses with the tip. In connection with first principles simulations we can determine the orientation and position of the pristine molecules as well as adsorbed mono- and diradicals and the halogens. In particular, for the radicals we observe strongly twisted and bent 3D adsorption structures.

O 83.9 Thu 17:15 H9

Complex Probe Particle Model Simulations Supporting nc-AFM Experiments — ●ONDREJ KREJCI¹, FABIAN SCHULZ^{1,2}, JUHA RITALA¹, ARI P. SEITSONEN³, PETER LILJEROTH¹, SHIGEKI KAWAI⁴, REMY PAWLAK⁵, FENG XU⁶, LIFEN PENG⁶, AKIHIRO ORITA⁶, ERNST MEYER⁵, TOMIHIKO NISHIUCHI⁷, KEISUKE SAHARA⁷, TAKUYA KODAMA⁷, TAKASHI KUBO⁷, and ADAM S. FOSTER^{1,8,9} — ¹Aalto Uni., Espoo, Fin. — ²IBM Zurich, Swi. — ³Ecole Normale Supérieure, Paris, Fra. — ⁴NIMS, Tsukuba, Jap. — ⁵Uni. of Basel, Swi. — ⁶Okayama Uni. of Science, Okayama, Ja. — ⁷Osaka Uni., Toyonaka, Jap. — ⁸Kanazawa Uni., Kanazawa, Jap. — ⁹Johannes Gutenberg Uni., Mainz, Ger.

I will present simulations of systems studied experimentally with a CO-tip AFM/STM and development of the probe particle AFM model. [1,2] The presentation will also contain description of the experiments and DFT calculations of the systems: The first is hBN/Ir(111). Unexpected contrast was observed in CO-tip AFM images. Complex electrostatics of the tip [3] helped us to understand the origin of the contrast. [4] The other systems are non-planar molecules adsorbed on Cu(111) and Au(111). More realistic description of the CO tip, [5] were found to be important for better agreement between simulations and experiments on these molecules. [6]

[1] Hapala et al. PRB 90, 085421, 2014. [2] Hapala et al. PRL 113, 226101, 2014. [3] Ellner et al. Nano Lett. 16, 1974, 2016. [4] Schulz et al. ACS Nano 12, 5274, 2018. [5] Di Giovannantonio et al. JACS 140, 3532, 2018. [6] Kawai et al. ACS Nano 12, 8791, 2018.