

O 34: Nanostructures at Surfaces II

Time: Tuesday 10:30–12:30

Location: H6

O 34.1 Tue 10:30 H6

Hydrogen-bonded bimolecular network on Au(111) — •CHRISTIAN STEINER¹, ZECHAO YANG¹, UTE MEINHARDT², BETTINA GLIEMANN², MARTIN GURRATH³, BERND MEYER³, MILAN KIVALA², and SABINE MAIER¹ — ¹Department of Physics, FAU Erlangen-Nürnberg, Germany — ²Department of Chemistry and Pharmacy, FAU Erlangen-Nürnberg, Germany — ³Computer-Chemie-Centrum, FAU Erlangen-Nürnberg, Germany

Understanding and controlling the formation of multi-component molecular self-assemblies is important for the design of donor-acceptor networks which are an integral part of organic optoelectronic devices. We discuss the self-assembly and electronic properties of monomolecular[1] and bimolecular networks assembled from carboxyl- and diaminotriazinyl-functionalized triphenylamine derivatives based on low-temperature scanning tunneling microscopy experiments and density functional theory calculations. On Au(111), both molecules arrange in large porous hydrogen-bonded networks in order to optimize the intermolecular hydrogen bonding. Upon co-adsorption, the molecules form perfectly ordered bimolecular honeycomb networks stabilized by bonds between the carboxyl and the diaminotriazinyl groups. The HOMO-LUMO gap in the mixed network is defined by the two types of molecules, which is typical for an electron donor-acceptor scheme.

[1] C. Steiner et al. *J. Phys. Chem. C*, 119 (46), 25945-25955 (2015)

O 34.2 Tue 10:45 H6

Self-assembling and chemistry of ferrocene dicarboxylic acid on different substrates — •JAN BERGER¹, OLEXANDR STETSOVYCH¹, KRZYSZTOF KOŚMIDER¹, MARTIN VONDRÁČEK², MARTIN ŠVEC¹, and PAVEL JELÍNEK¹ — ¹Institute of Physics, Academy of Sciences of the Czech Republic, Cukrovarnická 10, CZ-16200, Prague, Czech Republic — ²Institute of Physics, Academy of Sciences of the Czech Republic, Na Slovance 1999/2, CZ-18221, Prague, Czech Republic

Ferrocene based molecules are extremely appealing as they provide the possibility of having built-in spin or charge functionalities. However there are only limited studies of structural and electronic properties on surfaces so far. We investigated self-assembling processes of ferrocene-based molecules on both metallic (Ag(111), Cu(110)) and insulating (Cu₃N/Cu(110)) with high-resolution AFM/STM combined with XPS and NEXAFS. The experimental evidence is corroborated with total energy DFT calculations and advanced AFM simulations. The analysis of the data allows understanding of the unique arrangement and adsorption geometry of the molecules on each substrate, as well as the chemical changes of the carboxylic groups. Where the molecules on the Ag(111) show only a weak interaction with the substrate and a complex self-assembling configuration. On the Cu(110) and Cu₃N/Cu(110) the carboxylic groups are a subject to dehydrogenation forming strong chemical bond to the substrate onto the Cu atoms, keeping an upright orientation of the ferrocene cyclopentadiene rings.

O 34.3 Tue 11:00 H6

On-surface synthesis of covalent organic nanostructures on metals and strategies for post synthetic decoupling — •ATENA RASTGOO LAHROOD^{1,2}, JONAS BJÖRK³, MATTHIAS LISCHKA^{1,2}, JOHANNA EICHHORN^{1,2}, WOLFGANG M. HECKL^{1,2,4}, and MARKUS LACKINGER^{1,2,4} — ¹Department of Physics, Tech. Univ. Munich, James-Frank-Str. 1, 85748 Garching — ²Center for NanoScience (CeNS), Schellingstr. 4, 80799 Munich — ³Department of Physics Chemistry and Biology, IFM Linköping University, 58183 Linköping, Sweden — ⁴Deutsches Museum, Museumsinsel 1, 80538 Munich

On-surface polymerization is a versatile approach for the synthesis of otherwise inaccessible extended low-dimensional organic nanostructures. Ullmann coupling as the most favored reaction relies on the reactivity of metal surfaces to initiate the coupling by dissociating halogen substituents. Since the metal surfaces that are indispensable for the synthesis are unfavorable for many applications, we explore strategies for a post synthetic detachment.

Surface chemical studies of 1,3-diiodobenzene on Cu(111) revealed covalently coupled trimers as reaction products adsorbed atop a closed iodine monolayer rather than directly on the metal surface. These unexpected results suggest iodine adsorbs underneath the or-

ganics, thereby indicating possibilities for using iodine monolayers for post_synthetic decoupling.

This approach was verified by exposing on-surface synthesized covalent porous 2D polyphenylene networks to iodine vapor. Samples were characterized by STM, XPS, and NEXAFS.

O 34.4 Tue 11:15 H6

On-surface synthesis of non-symmetric molecular nodes — •CHRISTOPHE NACCI¹, FRANCISCO AMPLÉ², ANDREAS VIERTEL³, STEFAN HECHT⁴, CHRISTIAN JOACHIM⁵, and LEONHARD GRILL⁶ — ¹Department of Physical Chemistry, University of Graz, Austria — ²IMRE, Singapore — ³Department of Chemistry, Humboldt-Universität zu Berlin, Germany — ⁴Department of Chemistry, Humboldt-Universität zu Berlin, Germany — ⁵CEMES-CNRS, Toulouse, France — ⁶Department of Physical Chemistry, University of Graz, Austria

On-surface synthesis is a promising strategy for building complex molecular architectures that are potentially relevant in the field of molecular electronics. Suitable design of molecular building blocks is required in order to assemble functional molecules into stably bound networks with a well-defined spatial arrangement. In this presentation low-temperature scanning tunneling microscopy and spectroscopy are used to image individual molecules and determine their electronic properties at surface with high spatial resolution. Non-symmetric molecular nodes comprised of central molecule and equipped with short polyfluorene wires at predefined positions were grown by on-surface synthesis. The asymmetric node structure is highly desired since it encodes different conjugated pathways, i.e. potentially different electrical channels. The assembly of different molecular nodes will be discussed as well as the electrical characterization of individual non-symmetric molecular nodes by pulling them off a supporting surface with the tip of a scanning tunneling microscope.

O 34.5 Tue 11:30 H6

Interplay of chemical and electronic structure on the single-molecule level in 2D polymerization — •CLAUDIUS MORCHUTT^{1,3}, JONAS BJÖRK², CAROLA STRASSER³, ULRICH STARKE³, RICO GUTZLER³, and KLAUS KERN^{1,3} — ¹Max Planck Institute for Solid State Research, Heisenbergstrasse 1, 70569 Stuttgart, Germany — ²Department of Physics, Chemistry and Biology, IFM, Linköping University, 58183 Linköping, Sweden — ³Institut de Physique de la Matière Condensée, Ecole Polytechnique Fédérale de Lausanne, 1015 Lausanne, Switzerland

Single-layers of covalently-linked organic materials in the form of two-dimensional (2D) polymers constitute structures complementary to inorganic 2D materials. The electronic properties of the 2D polymer can be manipulated through a deliberate choice of precursor organic molecules. In this work, the changes in electronic structure from precursor molecule to oligomer are addressed by scanning tunneling spectroscopy and ultra violet photoelectron spectroscopy. The polymerization reaction of 1,3,5-tris(4-carboxyphenyl)benzene via reductive decarboxylation on Cu(111) is investigated by scanning tunneling microscopy, x-ray photoelectron spectroscopy and density functional theory calculations. We present a comprehensive study of an on-surface coupling reaction without contaminating side-products and we show HOMO/LUMO shifts as a consequence of decarboxylation and polymerization on the molecular level.

O 34.6 Tue 11:45 H6

Templated bilayer self-assembly of fully conjugated π -expanded macrocyclic oligothiophenes complexed with fullerenes — •JOSE D. COJAL GONZALEZ¹, MASAAHIKO IYODA², and JÜRGEN P. RABE¹ — ¹Department of Physics & IRIS Adlershof, Humboldt-Universität zu Berlin, Berlin — ²Department of Chemistry, Graduate School of Science and Engineering, Tokyo Metropolitan University, Hachioji, Tokyo

Fully conjugated π -expanded macrocyclic oligothiophenes have been envisaged for host-guest systems, as building blocks for supramolecular nanostructures and photovoltaic applications due to their structural, optical and electronic properties. However, control over the self-assembly of such systems still remains a challenge. Here, we report a self-assembled monolayer of hydrogen-bonded trimesic acid at

the interface between its heptanoic acid solution and highly oriented pyrolytic graphite. This monolayer is shown to provide host-sites for the epitaxial ordering of Saturn-like complexes of fullerenes with π -expanded oligothiophene macrocycles(1) in mono- and bilayers. The bilayer and triple layer formation was confirmed by STM tomography, based on discrete bias set-point imaging of each layer. All force-field potential interaction energy calculations confirmed the stability of the multilayer architecture. Finally, Scanning Tunneling Spectroscopy (STS) of the layers allowed for determination of the rectification characteristics and the position of the combined frontier orbitals.

(1) Shimizu H, Cojal Gonzalez JD, Hasegawa M, Nishinaga T, Haque T, Takase M, Otani H, Rabe JP and Iyoda M 2015 *J. Am. Chem. Soc.* **137**, 3877-3885

O 34.7 Tue 12:00 H6

A comparative study of two perylene derivatives on Cu(111): insight into the bonding mechanism — ●MIHAELA ENACHE¹, MANFRED MATENA², JONAS BJÖRK³, JORGE LOBO-CHECA⁴, THOMAS JUNG², MATS PERSSON⁵, and LUTZ GADE⁶ — ¹University of Groningen, Groningen, Netherlands — ²University of Basel, Basel, Switzerland — ³University of Linköping, Linköping, Sweden — ⁴Centro de Física de Materiales (CSIC-UPV-EHU), San Sebastian, Spain — ⁵University of Liverpool, Liverpool, UK — ⁶Universität Heidelberg, Heidelberg, Germany

Herein, an experimental and theoretical characterization of the adsorption of two perylene derivatives on Cu(111) is presented [1, 2]. The main focus of this work lies on the analysis of molecule-molecule and molecule-substrate interactions by combining results from scanning tunneling microscopy, x-ray photoelectron spectroscopy, x-ray standing wave (XSW) measurements, and density functional theory.

For submonolayer coverage and after annealing (>150°C), both systems form a metal-coordinated network, which is commensurate to the

substrate. By performing XSW measurements, the vertical adsorption geometry was determined and thereby, insight into the interplay between intermolecular and molecule-substrate interactions was gained. As a result of the metal coordination, the molecule-substrate interactions are decreased and the molecules are essentially decoupled from the Cu(111) surface.

[1] M. Matena et al., *Phys. Rev. B*, **90**, 125408 (2014)

[2] M. Matena et al., *Chem. Eur. J.*, **16**, 2079 (2010)

O 34.8 Tue 12:15 H6

On-surface fabrication of acenes — ●JUSTUS KRÜGER¹, NIKO PAVLIČEK², FRANK EISENHUT¹, JOSÉ M. ALONSO³, DOLORES PÉREZ³, ENRIQUE GUITIÁN³, THOMAS LEHMANN², DMITRY RYNDYK², ANDRÉ GOURDON⁴, GERHARD MEYER², LEO GROSS², DIEGO PEÑA³, GIANAURELIO CUNIBERTI¹, and FRANCESCA MORESCO¹ — ¹Institute for Materials Science, Max Bergmann Center of Biomaterials, and Center for Advancing Electronics Dresden, TU Dresden, 01069 Dresden, Germany — ²IBM Research-Zurich, 8803 Rüschlikon, Switzerland — ³CIQUS and Departamento de Química Orgánica, Universidade de Santiago de Compostela. Santiago de Compostela 15782, Spain — ⁴CEMES, UPR 8011 CNRS, Nanosciences Group, 29 Rue J. Marvig, P.O. Box 94347, 31055 Toulouse, France

We present the on-surface reduction of acene-derivatives to form genuine acenes (hydrocarbons with linearly fused benzene rings) on Au(111) and Cu(111). The conversion is achieved by scanning tunneling microscopy (STM) tip-induced manipulation as well as thermal activation and is conclusively demonstrated by means of atomic force microscopy with atomic resolution. This observed transformation may pave the way for the on-surface preparation and stabilization of even higher acenes.