

O 111: Nanostructures at Surfaces: Molecular Systems III

Time: Friday 10:30–13:00

Location: REC/PHY C213

O 111.1 Fri 10:30 REC/PHY C213

Resolving molecular products of astro-photochemistry: light-induced hydrogenation of 1,2-bis(2-phenylethynyl)benzene —•MARTIN SVEC¹, JACK HELLERSTEDT¹, ALES CAHLIK¹, OLEKSANDR STETSOVYCH¹, MARIA MORO LAGARES¹, IRENA STARA², IVO STARY², and PAVEL JELINEK¹ — ¹Institute of Physics, CAS, Praha, CR — ²Institute of Chemistry and Biochemistry, CAS, Praha, CR

The interaction between photons and molecules is as enticing as it is elusive. Typically, light-induced reactions have complicated reaction pathways and a diverse range of products that are difficult to characterize with (liquid) solution based measurements. The advent of on-surface preparation and scanned probe measurement techniques has greatly advanced the ability to resolve complicated reactions by direct observation of structural and conformational changes. We extend this a step further by considering the possibility of reactions occurring in the dilute limit, e.g. high and ultrahigh vacuum (UHV) conditions, the nearest local approximation of the interstellar medium of our universe.

In this paradigmatic astro-photochemistry experiment, a dilute gas (in UHV) of phenyl-based molecules (1,2-bis(2-phenylethynyl)benzene) is exposed to high intensity UV light during deposition onto a single crystal metal substrate. The products are subsequently studied via low temperature (5K) scanning probe techniques capable of resolving molecular structure at the atomic level. We observe chemically altered products, assembled in geometrically distinct superstructures. Linear assemblies can exceed 250nm in length. These are identified using theoretical simulations and comparison with the AFM/STM data.

O 111.2 Fri 10:45 REC/PHY C213

Pyridyl-functionalized triarylamines self-assembled on Au(111) —•LEONID SOLIANYK¹, JUAN CARLOS MORENO-LÓPEZ¹, JUN LI¹, STEFANO GOTTARDI¹, MIHAELA ENACHE¹, UTE MEINHARDT², MILAN KIVALA², and MEIKE STÖHR¹ — ¹Zernike Institute for Advanced Materials, University of Groningen, The Netherlands — ²Department of Chemistry and Pharmacy, University of Erlangen-Nürnberg, Germany

Engineering of molecular nanostructures on well-defined inorganic surfaces is essential for the development of nanoelectronic devices. In order to build up the nanostructures with atomic precision, ultimate control over the underlying interactions is needed. In our work, we investigated the self-assembly of pyridyl-functionalized triarylamines on Au(111) by scanning tunneling microscopy (STM), X-ray photoelectron spectroscopy (XPS) and low energy electron diffraction (LEED). For deposition of submonolayer coverage onto Au(111) held at room temperature, a close-packed phase as well as a hexagonal nanoporous network were observed to co-exist. The close-packed phase is stabilized by hydrogen bonding while the nanoporous network is held together by metal-ligand interactions with native gold atoms. Thermal annealing at 180°C results in the exclusive formation of a second Au-coordinated hexagonal nanoporous network with a larger pore size. Based on STM and LEED data the structural models and the intermolecular as well as molecule-substrate interactions will be discussed. Moreover, XPS data add information about the chemical state of the structures and corroborate the findings.

O 111.3 Fri 11:00 REC/PHY C213

Controlled On-Surface Synthesis of Organic and Organometallic Macrocycles —•QITANG FAN¹, TAO WANG², CICI WANG², JUNFA ZHU², MIN CHEN¹, MALTE ZUGERMEIER¹, CLAUDIO K. KRUG¹, JULIAN KUTTNER¹, GERHARD HILT¹, and J. MICHAEL GOTTFRIED¹ — ¹Fachbereich Chemie, Philipps-Universität Marburg, Germany — ²National Synchrotron Radiation Laboratory, University of Science and Technology of China

Macrocycles and cyclic polymers have properties distinctly different from those of their linear counterparts. While effective approaches for their synthesis in solution remain scarce, on-surface synthesis has proven to be a viable alternative due to the inherent template effects. The controlled formation of hyperbenzene and organometallic macrocycles has been achieved on (modified) metal surfaces from 4,4'-dibromo-m-terphenyl (DBMTP) precursor molecules. Hyperbenzene, a hexagon consisting of 18 phenyl rings, forms on Cu(111), Ag(111) and Au(111) with different yields, which are maximized under pseudo-high dilution conditions. On clean Cu(110), DBMTP reacts to form

zigzag organometallic chains linked with C-Cu-C bonds. However, with a template based on a Cu(110)-(2 x 1)O supergrating, cyclic organometallic tetragons and hexagons are obtained on the Cu stripes (with width from 2.6 nm to 3.6 nm). These methods may pave the way for the synthesis of other macrocycles.

O 111.4 Fri 11:15 REC/PHY C213

On-surface synthesis and characterization of nonsymmetrical single-molecule nodes —•CHRISTOPHE NACCI¹, ANDREAS VIERTEL², STEFAN HECHT², and LEONHARD GRILL¹ — ¹University of Graz, Graz, Austria — ²Humboldt-University, Berlin, Germany

On-surface reactions are a promising strategy for synthesizing complex molecular architectures that are potentially relevant in the field of novel nanostructures and molecular electronics. Suitable design of molecular building blocks is required to construct molecular nanostructures with a well-defined size, geometry and composition [1]. A molecular node, i.e. a junction where several molecular wires merge, represents a key component in monomolecular electronic circuits, but its growth requires a precise and well-defined arrangement of different building blocks. Here, we report the first construction of a chemically and geometrically well-defined covalent architecture made of one central node and three molecular wires arranged in a non-symmetrical fashion in order to ensure different conjugation pathways [2]. Slight modifications of the molecular building blocks results in significant change of the outcome of the chemical reactions involved in the on-surface synthesis process on the Au(111) surface. The electrical characterization of individual non-symmetric molecular nodes by pulling them off a supporting surface with the tip of a scanning tunneling microscope will be discussed [2]. [1] L. Grill et al., *Nature Nanotechnology* **2**, 687 (2007) [2] C. Nacci et al., *Angew. Chem. Int. Ed.* **55**, 13724 (2016)

O 111.5 Fri 11:30 REC/PHY C213

Structural analysis of small carbon cage molecules with low temperature scanning probe microscopy —•JALMAR TSCHAKERT¹, DANIEL EBELING¹, MARVIN STIEFERMANN¹, MARINA SEKUTOR², PETER SCHREINER², and ANDRÉ SCHIRMSEIN¹ — ¹Institute of Applied Physics - Justus Liebig University, Gießen, Germany — ²Institute of Organic Chemistry - Justus Liebig University, Gießen, Germany

Diamonoids are small hydrogen terminated carbon cage molecules that are composed of one or more unit cages of the diamond lattice. Self-assembled monolayers of such molecules are known for their outstanding electronic properties [1,2]. Here we study the self-assembly process of tetramantane molecules (i.e., a diamonoid that consists of four diamond unit cages) on Cu(111) and Au(111) surfaces by low temperature atomic force microscopy with CO-functionalized tips. This allows us to determine the precise orientation and arrangement of the adsorbed molecules within 2D islands, which gives new insight into the underlying mechanism of the self-assembly process of these molecules.

[1] *Science* **316**, 1460-1462 (2007)[2] *Nature Nanotechnology* **11**, 267-272 (2016)

O 111.6 Fri 11:45 REC/PHY C213

Photophysical properties of semiconducting armchair-edge graphene nanoribbons —•SEYED KHALIL ALAVI^{1,2}, MARKUS PFEIFFER¹, BORIS SENKOVSKIY³, ANDREA BLIESENER³, JINGYI ZHU³, SAMUEL MICHEL³, ALEXEI V. FEDOROV⁴, RAPHAEL GERMAN³, DIRK HERTEL¹, DANNY HABERER⁴, LUCA PETACCIA⁵, FELIX R. FISCHER⁴, KLAUS MEERHOLZ¹, PAUL VAN LOOSDRECHT³, ALEXANDER GRÜNEIS³, and KLAS LINDFORS¹ — ¹Department of Chemistry, University of Cologne, Luxemburger Str. 116, 50939 Köln, Germany — ²Institut für Angewandte Physik der Universität Bonn, Wegelerstr. 8, 53115, Bonn, Germany — ³II. Physikalisches Institut, Universität zu Köln, Zùlpicher Strasse 77, 50937 Köln, Germany — ⁴Department of Chemistry, University of California at Berkeley, Tan Hall 680, Berkeley, CA 94720, USA — ⁵Elettra Sincrotrone Trieste, Strada Statale 14 km 163.5, 34149 Trieste, Italy

Armchair graphene nanoribbons are novel one-dimensional semiconductors with well defined structure and promising optoelectronic properties. We present here for the first time observation of fluorescence from graphene nanoribbons and photophysical characterization for

aligned nanoribbons on insulating substrates. We further determine the excitonic resonances in the material by wavelength dependent Raman spectroscopy. From photoluminescence measurements we obtain polarized non-bleaching emission that is excited by light polarized along the ribbon. We observe a clear spectral shift from the position of the lowest exciton. The emission is attributed to bright defects in the material, which is demonstrated by controlled photochemical induction.

O 111.7 Fri 12:00 REC/PHY C213

Substrate mediated electronic interactions of organic charge-transfer complexes on Ag(111) — ●KATHRIN MÜLLER¹, NICO SCHMIDT², STEFAN LINK¹, MICHAEL GRUNST³, RENE RIEDEL³, WALTER MALONE⁴, ABDELKADER KARA⁴, ULRICH STARKE¹, MILAN KIVALA³, and MEIKE STÖHR² — ¹Max Planck Institute for Solid State Research, Stuttgart, Germany — ²Zernike Institute for Advanced Materials, University of Groningen, Netherlands — ³Department of Chemistry and Pharmacy University Erlangen-Nürnberg, Germany — ⁴Department of Physics University of Central Florida Orlando, USA

The use of organic molecules in electronic devices is gaining increasing interest due to their low cost, flexibility and easy processability. However, organic molecules often show weak intermolecular interactions limiting the charge carrier mobility. The use of electronically complementary molecules, which exhibit strong intermolecular interaction, might overcome this problem. Here we report on the self-assembly and the electronic properties of two complementary molecules containing electron-withdrawing and -donating cyano- and methoxy-groups, respectively, on Ag(111). The investigations of the structural and electronic properties of homogeneous layers containing only one species as well as heterogeneous layers containing both were carried out by STM, STS, XPS, ARPES, UPS, LEED and DFT calculations. The molecules are strongly interacting with each other leading to an alignment of the lowest unoccupied molecular orbitals (LUMOs). However, we also observe strong molecule/substrate interactions and thus we speculate that the LUMO alignment is mediated by the metallic substrate.

O 111.8 Fri 12:15 REC/PHY C213

Imaging on-surface hierarchical assembly of chiral organometallic polymers — ●LAERTE L. PATERA^{1,2,3}, ZHIYU ZOU^{2,4}, CARLO DRI^{2,3,5}, CRISTINA AFRICH², JASCHA REPP¹, and GIOVANNI COMELLI^{2,3} — ¹Institute of Experimental and Applied Physics, University of Regensburg, 93053 Regensburg, Germany — ²IOM-CNR Laboratorio TASC, Area Science Park, 34149 Trieste, Italy — ³Department of Physics, University of Trieste, 34127 Trieste, Italy — ⁴Abdus Salam International Centre for Theoretical Physics, 34151 Trieste, Italy — ⁵Elettra - Sincrotrone Trieste S.C.p.A., 34149 Trieste, Italy

We report the first real-time observation of the self-assembly mechanisms driving the hierarchical expression of supramolecular chirality, for 10,10'-dibromo-9,9'-bianthryl on Cu(111). Molecular recognition steers a multi-level chirality transfer, leading first to the growth of chiral organometallic chains and then to the formation of enantiopure islands. The structure of the polymeric networks has been determined by means of non-contact atomic force microscopy (nc-AFM), while high-speed scanning tunnelling microscopy (STM) revealed details of the surface kinetics. The direct observation of the assembly mechanisms allowed us to evaluate the enantioselectivity of the interchain coupling, shedding light on the driving forces of the hierarchical chi-

rality expression. Our results provide an extended characterization of processes involved in the sequential self-assembly of enantiopure structures, paving the way for the design of functional supramolecular architectures.

O 111.9 Fri 12:30 REC/PHY C213

Imaging the electronic structure of on-surface generated acenes — ●JUSTUS KRÜGER¹, FRANK EISENHUT¹, THOMAS LEHMANN¹, JOSÉ M. ALONSO², DMITRY SKIDIN¹, DOLORES PÉREZ², ENRIQUE GUTIÁN², DMITRY A. RYNDYK¹, CHRISTIAN JOACHIM³, DIEGO PEÑA², FRANCESCA MORESCO¹, and GIANAURELIO CUNIBERTI¹ — ¹Institute for Materials Science, Max Bergmann Center of Biomaterials, and Center for Advancing Electronics Dresden, TU Dresden, 01069 Dresden — ²CIQUS and Departamento de Química Orgánica, Universidade de Santiago de Compostela. Santiago de Compostela 15782 — ³GNS & MANA Satellite, CEMES, CNRS, 29 rue J. Marvig, 31055 Toulouse Cedex

We present the fabrication of acenes (polycyclic hydrocarbons formed by the linear fusion of several benzene rings) on metallic surfaces. In particular, scanning tunneling microscopy and spectroscopy of single hexacene molecules is performed to directly visualize the frontier orbital resonances and to capture their narrow energy gap. Due to the high reactivity of hexacene under ambient conditions, scanning probe investigations at the single molecule level could not be obtained so far. In this work, we proof the scalability of a recently introduced on-surface reaction [1] to generate and stabilize hexacene directly on Au(111) by making use of oxygen-containing precursors. In the last part of this talk, we analyze the electronic resonances of long acenes on Au(111) as function of their length. [1] ACS Nano, 2016, 10 (4), pp 4538-4542

O 111.10 Fri 12:45 REC/PHY C213

Thermal Fluctuations of Structured Adhered Bio-Membranes Probed with Nanometer/Microsecond Resolution — ●CORNELIA MONZEL^{1,2,3}, DANIEL SCHMIDT^{4,5}, ANA-SUNCANA SMITH⁴, UDO SEIFERT⁵, KHEYA SENGUPTA², and RUDOLF MERKEL¹ — ¹Forschungszentrum Jülich, Germany — ²Centre Interdisciplinaire de Nanoscience de Marseille, France — ³present address: Institut Curie, France — ⁴Friedrich-Alexander Universität Erlangen-Nürnberg, Germany — ⁵Universität Stuttgart, Germany

Bio-membrane adhesion is essential for life and understanding its physical basis is key for further insight into many vital processes. Here, we explore bio-membrane adhesion to heterogeneously distributed linkers, as mimicked by micropatterns of adhesive and nonadhesive regions. As bio-membrane, we use closed lipid shells, so-called giant unilamellar vesicles (GUV) which bind to the patterned linkers, but, intriguingly, exhibit a fluctuating membrane within nonadhesive regions. The thermally excited fluctuations result in an entropic repulsion spatially separating the membrane from the substrate. Additional attractive and repulsive interactions near the substrate determine the final shape of the membrane, which we explore using different adhesion pattern and applying osmotic pressure changes. We further advance Reflection Interference Contrast Microscopy and develop Dynamic Optical Displacement Spectroscopy to monitor membrane undulations with up to 4nm and 10⁻⁶s resolution. From the analysis of this data and by expanding the theoretical framework a coherent view of this structured adhered membrane and its surface interaction is obtained.