

O 97: Nanostructures at Surfaces: Molecular Systems II

Time: Thursday 15:00–18:30

Location: REC/PHY C213

Invited Talk O 97.1 Thu 15:00 REC/PHY C213
The challenge of atomic resolution in liquid and ambient conditions with AFM — ●ALFRED J. WEYMOUTH — University of Regensburg, Germany

Since the invention of the atomic force microscope, there has been substantial drive to image in ambient and liquid environments. One challenge in these environments is atomic resolution. Keeping surfaces clean in vacuum, combined with cryogenic temperatures to lower both the instrumental noise and thermal drift, makes force microscopy easier. We have had great success with stiff sensors and frequency-modulation AFM. With these techniques, we are returning to the challenge of imaging samples in device- and biologically-relevant conditions.

We demonstrated atomic resolution with the qPlus sensor on KBr [1], and followed this with investigations on graphitic surfaces [2]. In order to better understand our data of HOPG we conducted a parallel investigation in UHV. We have also started to study biological samples: Working with Daniel Müller's group, we imaged a protein membrane in a liquid drop. More recently, we have imaged mica with atomic resolution in a liquid cell in a variety of solutions.

- [1] Wastl et. al., Phys. Rev. B, 87, 245415 (2013)
 [2] Wastl et. al., ACS Nano, 8, 5233 (2014)

Invited Talk O 97.2 Thu 15:30 REC/PHY C213
Single-molecule magnets: The influence of the surface — ●KATHARINA DILLER — Institute of Physics, École Polytechnique Fédérale de Lausanne (EPFL), Lausanne, Switzerland

A prerequisite for using magnetic nanostructures in data storage applications is magnetic remanence, i.e., magnetization after removal of an external magnetic field. Single-molecule magnets are metal-organic compounds which (below a certain blocking temperature) possess this property. However, the interaction with the environment often leads to fast relaxation of the magnetization, a problem especially prevalent for single-molecule magnets adsorbed on metal supports. Using the example of terbium phthalocyanine double decker (TbPc₂) molecules we will discuss the influence of the surface on the magnetic and electronic properties of the adsorbates. The TbPc₂ molecules are either deposited by molecular beam epitaxy onto the substrate of choice or are directly created by on-surface metallation, which allows us to selectively probe different scenarios. Using a combination of scanning tunnelling microscopy and X-ray absorption spectroscopy, we show how different decoupling layers enhance the magnetic remanence of TbPc₂ and discuss which other factors influence the system.

O 97.3 Thu 16:00 REC/PHY C213
Self-assembly of cyano and pyridil functionalized molecules on epitaxial h-BN and metal supports — ●DOMENIK M. ZIMMERMANN¹, KNUD SEUFERT¹, JIRI KLIVAR², GAEL AMANS², IRENA G. STARÁ², IVO STARÝ², LUKA DORDEVIC³, TOMAS MARANGONI³, DAVIDE BONIFAZI³, JOHANNES V. BARTH¹, and WILLI AUWÄRTER¹ — ¹E20, Technische Universität München, Germany — ²Institute of Organic Chemistry and Biochemistry, Czech Academy of Sciences, Czech Republic — ³Department of Chemical and Pharmaceutical Sciences, University of Trieste, Italy

Functionality at the nanoscale is based on both, intrinsic properties of the basic building blocks like molecules or atoms and their modification due to interaction with the environment.

One such building block is helicene, an ortho-condensed polycyclic aromatic compound. Di-cyano, di-benzo functionalized helicenes feature a large in-plane dipole moment, favoring the formation of 1D chains along the high symmetry directions of a Ag(111) surface. In contrast the molecules assemble into large two-dimensional islands upon adsorption on h-BN/Cu(111). Another example is pyrene. Pyridil functionalized derivatives have shown distinct self-assembled structures, including arrays and kagome heterostructures[1]. On h-BN/Cu(111) these architectures can be electronically decoupled. Scanning tunneling spectroscopy is used to address their electronic properties to pave the way for potential optoelectronic applications.

- [1] T. Kaposi et al., ACS Nano 10, 7665 (2016).

O 97.4 Thu 16:15 REC/PHY C213
A comparative temperature-programmed XPS study of

surface-assisted Ullmann coupling on Au(111) vs. Ag(111) — ●MASSIMO FRITTON^{1,2}, DAVID DUNCAN¹, PETER DEIMEL¹, ATENA RASTGOO LAHROOD^{1,2}, FRANCESCO ALLEGRETTI¹, WOLFGANG M. HECKL^{1,2,3}, and MARKUS LACKINGER^{1,2,3} — ¹Department of Physics, TU München, James-Frank-Str. 1 — ²Center for NanoScience (CeNS), Schellingstr. 4 — ³Deutsches Museum, Museumsinsel 1

The intention of our study is to compare the kinetics of thermally activated Ullmann coupling of 1,3,5-Tris(4-bromophenyl)benzene on Au(111) vs. more reactive Ag(111) under ultrahigh vacuum conditions. Two aspects are studied here: activation by cleavage of halogen substituents as well as formation and conversion of reaction intermediates, i.e. organometallic networks. Therefore, we use temperature-programmed XPS (TP-XPS) in combination with STM. TP-XPS allows us to track the progression of dehalogenation, vs. temperature while heating due to chemical shifts of the Br 3d line. On Ag(111) debromination starts at 250 K and is completed at 300 K, while on Au(111) the dehalogenation occurs at higher temperature and over a more extended temperature range between 330 K and 460 K. STM images on both surfaces endorse the spectroscopic data. On Ag(111) the organometallic intermediates can easily be distinguished by the increased bond length and a bright feature corresponding to the C-Ag-C linkages. In contrast on Au(111) annealing directly leads to the covalent network formation.

O 97.5 Thu 16:30 REC/PHY C213
Host-guest chemistry in carbonyl functionalized pores of covalent structures on Au(111) — ●YI LIU¹, CHRISTIAN STEINER¹, MAXIMILIAN AMMON¹, NATALIE HAMMER², JULIAN GEBHARDT³, ANDREAS GÖRLING³, MILAN KIVALA², and SABINE MAIER¹ — ¹Department of Physics, University of Erlangen-Nürnberg, Erlangen, Germany — ²Chair of Organic Chemistry I, Department of Chemistry and Pharmacy, University of Erlangen-Nürnberg, Erlangen, Germany — ³Chair of Theoretical Chemistry, Department of Chemistry and Pharmacy, University of Erlangen-Nürnberg, Erlangen, Germany

Host-guest chemistry in nanoporous supramolecular networks physisorbed on solid surfaces is a rapidly expanding field owing to potential applications in separation technology, catalysis, and sensor devices. However, most structures rely on non-covalent interaction forces, which results in a lack of thermal stability and weak intermolecular transport.

We report on the host-guest interaction between atoms and molecules with carbonyl-functionalized pores in covalent networks. The covalent structures are obtained by on-surface synthesis of halogen-substituted carbonyl-bridged triphenylamines on Au(111). The templating effect of the pores was investigated by low-temperature scanning tunneling microscopy in combination with density-functional theory. We found that trimesic acid and halogen atoms can be trapped at specific sites in the pores through hydrogen bonds or van der Waals interaction, respectively. Interestingly, we observed that iodine-iodine interactions are preferred over iodine-carbonyl interactions.

O 97.6 Thu 16:45 REC/PHY C213
Electronic structure of one- and two-dimensional polymers fabricated in a hierarchical on-surface synthesis on Au(111) — CHRISTIAN STEINER¹, MAXIMILIAN AMMON¹, ZECHAO YANG¹, JULIAN GEBHARDT², ALEXANDER HEIDENREICH³, NATALIE HAMMER³, ANDREAS GÖRLING², MILAN KIVALA³, and ●SABINE MAIER¹ — ¹Department of Physics, University of Erlangen-Nürnberg, Erlangen, Germany — ²Chair of Theoretical Chemistry, Department of Chemistry and Pharmacy, University of Erlangen-Nürnberg, Erlangen, Germany — ³Chair of Organic Chemistry I, Department of Chemistry and Pharmacy, University of Erlangen-Nürnberg, Erlangen, Germany

The fabrication of nanostructures in a bottom-up approach from specific molecular precursors offers the opportunity to create tailored materials for applications in nanoelectronics. However, the formation of defect-free 2D covalent networks remains a challenge and makes it difficult to unveil their electronic structure.

Here, we report on the hierarchical on-surface synthesis of nearly defect-free 1D and 2D covalent architectures on Au(111), which were investigated by low-temperature scanning tunneling microscopy in combination with density-functional theory. The carbonyl-bridged triphenylamine precursors formed six-membered macrocycles and 1D

chains as intermediates in a Ullmann-type coupling reaction that were subsequently interlinked to 2D networks. We observed a reduction of the electronic band gap from the monomer to the 1D and 2D structures. The significant drop of the gap from the monomer to the polymer confirms an effective conjugation along the building blocks.

O 97.7 Thu 17:00 REC/PHY C213

Growth of Tm-based organometallic nanostructures on Gr/Ir(111) — ●STEFAN KRAUS¹, FELIX HUTTMANN¹, NICO ROTHENBACH², KATHARINA OLLEFS², LUCAS M. ARRUDA³, WOLFGANG KUCH³, HEIKO WENDE², and THOMAS MICHELY¹ — ¹Universität zu Köln, Germany — ²Universität Duisburg-Essen, Germany — ³Freie Universität Berlin, Germany

Organometallic compounds containing rare earth elements are of interest in molecular spintronics owing to the robust magnetic moment of the 4f ion. Here, we combine the lanthanide Tm with the organic molecule cyclooctatetraene (Cot) for the growth of organometallic nanostructures on Gr/Ir(111), obtaining three distinct phases (1)–(3). Synthesis on the undoped substrate yields (1) a disperse phase of repulsively interacting adsorbates. Based on its punctiform appearance it is presumed to consist of TmCot monomers which are stabilized by charge transfer into the substrate leading to a Coulomb repulsion between them. When surpassing a coverage of about 2% ML, (2) an island-forming “coffee bean” phase condenses out of (1) and coexists with it. Formation of (1) and (2) is inhibited by *n* doping of graphene via intercalation as further charge transfer is suppressed. Rather, synthesis on the doped substrate results in the formation of (3) sandwich-molecular wires growing in islands. Tuning the Tm/Cot ratio during growth controls the achievable wire length, in some islands exceeding 100 Tm ions per wire. Magnetic anisotropy from the action of the Cot ligand field on the Tm ion and the differing Tm separations in each phase are expected to yield a rich spectrum of magnetic properties.

O 97.8 Thu 17:15 REC/PHY C213

Trimethylsilyl protected alkyne precursors on metal surfaces — ●LIDING ZHANG¹, YI-QI ZHANG¹, ZHI CHEN², MATEUSZ PASZKIEWICZ¹, TAO LIN¹, MARIO RUBEN², JOHANNES BARTH¹, and FLORIAN KLAPPENBERGER¹ — ¹TU München, Physik E20, Garching, Deutschland — ²Karlsruher Institut für Technologie, Institute of Nanotechnology, Eggenstein-Leopoldshafen, Deutschland

We report on the application of trimethylsilyl(TMS) terminated alkyne precursors for opening new pathways for fabricating novel 1-D and 2-D carbon nano- materials on metal surfaces.

The commonly employed organic molecular beam epitaxy limits the weight of employed precursors as with increased weight, the temperature for evaporation can rise above the temperature required for intermolecular reactions. The chemical inertness of TMS protection groups inhibits intermolecular reactions and thus allows the evaporation of larger and heavier alkyne precursors.

All utilized TMS-protected alkyne precursors were successfully evaporated onto Cu, Au and Ag surfaces. Investigations with low temperature STM imaging show dense packed self-assembled supramolecular islands. Thermal annealing triggers TMS group cleave off and a subsequent two step reaction pathway reminiscent of on-surface Glaser coupling, allowing the formation of covalently bonded structures with varying degrees of structural regularity.

O 97.9 Thu 17:30 REC/PHY C213

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ent levels of inertness on different metal surfaces and triggers TMS group cleave off and a subsequent two step reaction pathway reminiscent of on-surface Glaser coupling, allowing the formation of covalently bonded structures with varying degrees of structural regularity.

O 97.10 Thu 17:45 REC/PHY C213

Solution-free synthesis of diboronic acid-derived COF monolayers on surfaces — ●SASKIA SPITZER^{1,2}, ATENA RASTGOO^{1,2}, VIKTORIA RITTER^{1,2}, WOLFGANG HECKL^{1,2,3}, and MARKUS LACKINGER^{1,2,3} — ¹Department of Physics, Tech. Univ. Munich, James-Franck-Str. 1, 85748 Garching — ²Center for NanoScience (CeNS), Schellingstr. 4, 80799 Munich — ³Deutsches Museum, Museumsinsel 1, 80538 Munich

Currently, surface-supported highly stable two-dimensional covalent organic frameworks (COF) with the highest structural qualities are achieved through condensation reactions as boronic acid dehydration. [1,2] The presence of water during the polymerization as equilibrium regulating agent induces bond reversibility. We combined this established approach with the merits of a solvent-free monomer deposition from the vapor phase. Thermal sublimation of larger diboronic acid monomers, due to their high reactivity, required an additional protection-deprotection-approach. The resulting networks were characterized on different length scales by a combination of light microscopy and Scanning Tunneling Microscopy, thus verifying the preparation protocol.

[1] J. F. Dienstmaier et al., ACS Nano, 5, 9737-9745 (2011)

[2] C. Z. Guan et al., Chem. Commun., 48, 2943-2945 (2012)

O 97.11 Thu 18:00 REC/PHY C213

The role of intrinsic vs. extrinsic adatoms for the formation of metal-organic structures from triphenylenehexamine: A comparative STM study on Ag(111) vs. Cu (111) — ●MATTHIAS LISCHKA¹, RENHAO DONG², MASSIMO FRITTON¹, WOLFGANG M. HECKL^{1,3}, XINLIANG FENG², and MARKUS LACKINGER^{1,3} — ¹Department of Physics, TU München, James-Franck-Str. 1, 85748 Garching — ²Department of Chemistry and Food Chemistry, and Center for Advancing Electronics TU Dresden, 01062 Dresden — ³Deutsches Museum, Museumsinsel 1, 80538 München

The thermally activated formation of metal-organic structures of triphenylenehexamine (THA) is comparatively studied on Ag(111) and Cu(111) under ultra high vacuum conditions. The structural characterization of each phase is carried out by high resolution scanning tunneling microscopy. On both pristine surfaces THA is initially partly deprotonated and directly forms metal-organic structures. On Ag(111) densely packed structures were observed, whereas on Cu(111) Cu-adatom coordinated hexamers were found. Upon progressive heating on Ag(111) no further structural change was observed until the desorption of THA. On Cu(111), however, further heating drives deprotonation of THA and results in a conversion of the Cu-adatom coordinated hexamers into trimers. A profound change was found on Ag(111) after additional deposition of Ni-atoms: moderate heating leads to porous networks that collapse into a more densely packed structure after annealing at higher temperatures.

O 97.12 Thu 18:15 REC/PHY C213

On-surface indene-formation by methyl bromide cleavage — ●FRANK EISENHUT¹, DMITRY SKIDIN¹, JUSTUS KRÜGER¹, THOMAS LEHMANN¹, ANDREAS VIERTTEL², SEDDIGHEH NIKKIPAR¹, DMITRY A. RYNDYK¹, STEFAN HECHT², FRANCESCA MORESCO¹, and GIANAURELIO CUNIBERTI^{1,3} — ¹Institute for Materials Science, Max Bergmann Center of Biomaterials, and Center for Advancing Electronics Dresden, TU Dresden, 01069 Dresden, Germany, — ²Department of Chemistry & IRIS Adlershof, Humboldt-Universität zu Berlin, Brook-Taylor-Straße 2, 12489 Berlin, Germany, — ³Dresden Center for Computational Materials Science (DCMS), TU Dresden, 01069 Dresden, Germany.

Manufacturing molecules with predefined structural and electronic properties is one of the central tasks in surface science nowadays. We investigate the thermal induced cyclization of dibromo-diphenylpyrene on Au(111) using scanning tunneling microscopy (STM) and spectroscopy.

We show that precursor molecules self-assemble on Au(111) and form by annealing intermediate structures assembled in characteristic dimers or tetramers. By further annealing the surface, we can cleave methyl bromide groups and synthesize diindeno-pyrene molecules, as shown by high resolution STM images and dI/dV maps of the electronic orbitals. Density functional theory (DFT) and electron scatter-

ing quantum chemistry (ESQC) calculations confirm the experimental | results.