

O 5: Nanostructures at Surfaces I: Organics

Time: Monday 10:30–13:00

Location: H15

O 5.1 Mon 10:30 H15

Ring/Chain Competition in Organometallic Oligomers with Non-Alternant Aromatic Building Blocks — ●CLAUDIO K. KRUG¹, QITANG FAN¹, DAMIAN NIECKARZ², FLORIAN FILLSACK¹, JOHANNES GLOWATZKI¹, NICOLE TREBEL¹, LUKAS J. HEUPLICK¹, TABEA KOEHLER¹, PAWEŁ SZABELSKI², and J. MICHAEL GOTTFRIED¹ — ¹Philipps-Universität Marburg, Fachbereich Chemie, Hans-Meerwein-Str. 4, 35032 Marburg, Germany — ²Department of Theoretical Chemistry, Maria Curie-Skłodowska University, Pl. M.C. Skłodowskiej 3, Lublin 20-031, Poland

Organometallic oligomers with C-Cu-C bonds are formed from the non-alternant aromatic compound 1,3-dibromoazulene (DBAz) after deposition on a Cu(111) surface. The oligomers appear either as macrocycles (mostly hexamers) or as chains. Depending on the DBAz coverage and the annealing temperature, the ratio between rings and chains can be tuned by kinetic and thermodynamic control. We have studied the ring/chain competition by statistical analysis of scanning tunneling microscopy (STM) images. Upon deposition at 300 K, the structure formation is kinetically controlled, resulting in the formation of mostly regio-irregular chains. Annealing these chains to temperatures above 390 K switches the conditions to thermodynamic control, which leads to an increased yield of the thermodynamically more stable macrocycles. In the low-coverage limit, almost 80% of the deposited monomers are incorporated in cyclic hexamers. These experimental results are compared to Monte Carlo (MC) simulations, which confirm the influences of kinetic and thermodynamic control.

O 5.2 Mon 10:45 H15

Real and k-space fingerprints of a temperature driven phase transition of TPT / Cu(111) — ●LU LYU¹, BENITO ARNOLDI¹, SINA MOUSAVION¹, SEBASTIAN BECKER^{1,2}, MANIRAJ MAHALINGAM¹, BENJAMIN STADTMÜLLER^{1,3}, and MARTIN AESCHLIMANN¹ — ¹Department of Physics, TU Kaiserslautern — ²Department of Chemistry, TU Kaiserslautern — ³Graduate School Materials Science in Mainz, Kaiserslautern

The design of 2D porous networks of organic molecules on metal surfaces has become a promising route to design multi-functional porous materials. Using VT-STM, LEED and Laser-ARPES, we investigate the geometric and electronic properties of monolayer 2,4,6-triphenyl-1,3,5-triazine (TPT) on Cu(111) for various sample temperatures. We find a continuously second-order phase transition in the temperature range of 297 K and 106 K, in which the TPT molecules transform from a close-packed structure to a well-ordered nanoporous-network. The mechanism can be understood by the thermodynamic competition between the intermolecular interactions (hydrogen-bonds of TPT peripheral phenyl groups) and the molecule-substrate interaction (central triazine N atoms with surface metal atoms). In the nanoporous-network phase, the standing wave of the electronic charge density can be observed in the cavities of the network in STM which coincides with the appearance of new parabolic surface states close to the Fermi level. Our findings provide a new insight into temperature-dependent electronic structures for 2D organic nanoporous-networks on noble metal surfaces.

O 5.3 Mon 11:00 H15

Molecularly resolved STM imaging of electron-induced cross-linking of aromatic self-assembled monolayers — ●PATRICK STOHMANN¹, SASCHA KOCH¹, YANG YANG¹, CHRISTOPHER DAVID KAISER¹, NIKLAS BIERE², and ARMIN GÖLZHÄUSER¹ — ¹Faculty of Physics, Physics of Supramolecular Systems and Surfaces, Bielefeld University, Universitätsstr. 25, 33615 Bielefeld, Germany — ²Faculty of Physics, Experimental Biophysics and Applied Nanoscience, Bielefeld University, Universitätsstr. 25, 33615 Bielefeld, Germany

When aromatic self-assembled monolayers (SAMs) are irradiated by electrons, intermolecular cross-linking leads to the formation of carbon nanomembranes (CNMs) with molecular thickness [1], making them ideal membranes for water purification [2]. Here, we focus on the structural transformation of a pristine 4-terphenylthiol (TPT) SAM on a Au(111) surface, investigated by scanning tunneling microscopy (STM). The irradiation with electrons was carried out by employing a focused electron beam of a scanning electron microscope (SEM) at 1keV, and, for comparison, a low-energy flood gun at 50eV. The use

of a combined STM/SEM microscope enables to acquire STM images before and after the irradiation steps without losing the probed sample area. We demonstrate that it is possible to study and image the initial steps of electron-induced cross-linking of the molecular layers. [1] A. Turchanin and A. Gözlhäuser, *Adv. Mat.* 2016, 28, 6075-6103 [2] Y. Yang et al., *ACS Nano* 2018, 12 (5), 4695-4701

O 5.4 Mon 11:15 H15

Coverage-dependent structural transformation of cyano-functionalized porphyrin networks on Au(111) via addition of cobalt atoms — ●BRIAN BAKER, NICO SCHMIDT, MIHAELA ENACHE, and MEIKE STÖHR — Zernike Institute for Advanced Materials, University of Groningen, Groningen, the Netherlands

The self-assembly process of a cobalt-porphyrin (Co-TCNPP) derivative containing cyanophenyl substituents at all four meso positions under ultrahigh vacuum on Au(111) was studied with room temperature scanning tunneling microscopy (STM) and low energy electron diffraction (LEED). Deposition of Co-TCNPP onto Au(111) gave rise to the formation of a close-packed H-bonded network, which was independent of coverage as revealed by STM and LEED. A coverage dependent behavior emerged upon metal-coordination with Co-atoms. At monolayer coverage, a reticulated network exhibiting a distinct four-fold Co-coordination was formed. By reducing the molecular coverage, a structural transformation took place. The four-fold Co-coordinated network was no longer an exclusive phase and coexisted with a second metal-organic coordination network (MOCN), i.e., a chevron structure stabilized by a simultaneous expression of H-bonding and three-fold Co-coordination. We attribute the coverage-dependent structural transformation to the in-plane compression pressure exerted by the molecules deposited on the surface. Therefore, a subtle interplay between the chemical nature of the building blocks and molecular coverage can steer the formation of topologically different MOCNs and opens an alternate pathway towards the fabrication of 2D networks.

O 5.5 Mon 11:30 H15

Confined states in self-assembled (OH)₂-pyrene porous networks on Ag(111) — ●PHILIPP D'ASTOLFO¹, RÉMY PAWLAK¹, CARL DRECHSEL¹, THILO GLATZEL¹, SILVIO DECURTINS², SHI-XIA LIU², and ERNST MEYER¹ — ¹Department of Physics, University of Basel, Klingelbergstrasse 82, Basel, CH 4056 — ²Department of Chemistry and Biochemistry, University of Bern, Freiestrasse 3, Bern, CH 3012

Quantum dots are known to confine electrons within their structure. Recently, porous networks obtained by assembling organic molecules on metal surfaces have also shown to confine the surface electrons into their cavities, forming an array of virtual quantum dots[1-3]. Here, we investigated 2,7-Dihydroxypyrene molecules, self-assembled onto an atomically flat Ag(111) surface, using scanning tunneling microscopy (STM) and atomic force microscopy (AFM) at 4K with CO-terminated tips. Two porous network morphologies are identified that are constituted by either pure 6-member pore assemblies or mixed assemblies of 6-, 8-, and 9-member pores. By comparing their electronic properties, we found a shift of the energy levels of the confinement depending on the pore size. Interestingly, 6-member pores in the mixed assembly exhibit a +30 meV higher energy than 6-member pores in the pure counterpart, despite having the same pore diameter.

[1] Piquero-Zulaica et al., *Nat. Comm.*, 2017, 8, 787.[2] Lobo-Checa et al., *Science*, 2009, 325, 300-303.[3] Klappenberger et al., *Phys. Rev. Lett.*, 2011, 106, 026802.

O 5.6 Mon 11:45 H15

Self-assembled monolayers of shape-persistent macrocycles on graphite: Coadsorption with fullerene derivatives — ●JOSHUA BAHR, ANNEMARIE MEYER, TRISTAN KELLER, SIGURD HÖGER, and STEFAN-SVEN JESTER — Kekulé-Institut für Organische Chemie und Biochemie der Rheinischen Friedrich-Wilhelms-Universität Bonn, Bonn, Deutschland

Shape-persistent arylene-alkynylene based macrocycles form self-assembled monolayers at the solid/liquid interface of highly oriented pyrolytic graphite and 1-phenyloctane. A flexible alkoxy side chain periphery increases the solubility of the macrocyclic species in common organic solvents, and mediates its assembly into highly robust

2D networks on the solid template. In the presence of fullerenes or derivatives thereof (providing - again - increased solubility), uniform domains containing both species are formed.[1] *In situ*-STM is used to gather insights into these 2D nanoscale systems *via* submolecularly resolved images. This work focuses on understanding the interplay between the macrocycle and fullerene derivative regarding the expected binding sites. [1] G.-B. Pan, X.-H. Cheng, S. Höger, W. Freyland, *J. Am. Chem. Soc.* **2006**, *128*, 4218-4219.

O 5.7 Mon 12:00 H15

Nanopatterns of molecular squares on graphite — KRISTIN GRATZFELD, NINA SCHÖNFELDER, TRISTAN J. KELLER, SIGURD HÖGER, and •STEFAN-SVEN JESTER — Kekulé-Institut für Organische Chemie und Biochemie, Universität Bonn, Gerhard-Domagk-Str. 1, 53121 Bonn, Germany

Supramolecular nanopatterns of arylene-alkynylene-macrocycles at the solid/liquid interface on HOPG are studied by scanning tunneling microscopy. We recently reported on self-assembled monolayers of *molecular squares* carrying pairs of OC₁₆H₃₃ side chains on all four sides.[1] Here, we present a series of molecules with a reduced (*i.e.* D_{2h}) symmetry: The (still) quadratic backbones carry pairs of long and short side chains of constant (OC₁₆H₃₃) and variable (OC_nH_{2n+1}, *n* = 6, 8, 10, 12) chain lengths, respectively. Chains of identical lengths are observed to interdigitate intermolecularly in ABAB packing schemes. Concentration dependent polymorphism is related to robust and less robust side chain packing. The more dense polymorphs are compared with monolayers of squares that carry only OC₁₆H₃₃ substituents on two opposing sides. The work is part of a supramolecular surface tiling strategy. [1] S.-S. Jester, E. Sigmund, S. Höger *J. Am. Chem. Soc.* **2011**, *133*, 11062.

O 5.8 Mon 12:15 H15

Self-assembly of para-hexaphenyl-dicarbonitrile on graphene — NICO SCHMIDT¹, JUN LI¹, •IDA DELAC MARION¹, MIHAELA ENACHE¹, STEFANO GOTTARDI¹, BRIAN BAKER¹, LEONID SOLIANYK¹, JUAN-CARLOS MORENO-LOPEZ¹, LETICIA MONJAS GOMEZ², ANNA HIRSCH², and MEIKE STÖHR¹ — ¹Zernike Institute for Advanced Materials, University of Groningen, Groningen, the Netherlands — ²Stratingh Institute for Chemistry, University of Groningen, Groningen, the Netherlands

We report on the self-assembly of para-hexaphenyl-dicarbonitrile (NC-Ph₆-CN) on epitaxial graphene on Cu(111) and Ir(111) as well as on highly oriented pyrolytic graphite (HOPG). Structural and electronic properties of the obtained assemblies were studied using STM, STS, and LEED. For NC-Ph₆-CN on graphene on both metallic substrates we found two related close-packed structures for which parallel molecules aligned in rows with a peculiar shift every fourth or fifth molecule, while for HOPG only one close-packed structure was observed. Hitherto the observed shift is a unique feature of NC-Ph₆-CN on graphitic substrates and already one layer of graphene is sufficient to induce it. Furthermore, we studied the formation of 1D and 2D metal-organic coordination (MOC) structures of NC-Ph₆-CN and Cu atoms on graphene on Ir(111). The dimensionality of the MOC struc-

tures was tuned by varying the stoichiometry between the NC-Ph₆-CN molecules and Cu atoms: for a 1:1 ratio, 1D chains based on two-fold Cu-coordination were formed, while for a 3:2 ratio, a 2D hexagonal porous network based on three-fold Cu-coordination was obtained.

O 5.9 Mon 12:30 H15

Self-assembled monolayers of molecular spoked wheels: Scanning tunneling microscopy — •TRISTAN J. KELLER, CHRISTOPHER STERZENBACH, JOSHUA BAHR, TARIA SCHNEIDERS, SIGURD HÖGER, and STEFAN-SVEN JESTER — Kekulé-Institut für Organische Chemie und Biochemie der Universität Bonn, Bonn, Deutschland

Imaging and modeling of shape persistent molecules is of great interest for 2D crystal engineering. In particular, the predictability of nanopatterns related to the molecular design and substitution pattern is a challenge. Here we report on the 2D supramolecular self-assembly of phenylene based molecular spoked wheels (MSWs). Scanning tunneling microscopy of monolayers of MSWs at the solid/liquid interfaces of highly oriented pyrolytic graphite (HOPG) and octanoic acid (OA) yields a submolecularly resolved insight into the adsorbate patterns. MSWs offer the unique opportunity to study truly shape-persistent macrocycles of well-defined geometry and symmetry. In particular MSWs with threefold rotational symmetry, and without any rotational symmetry could be investigated. Flexible alkoxy chains were used to stabilize the network formation on HOPG. The research aims at a detailed understanding of on-surface chirality of these compounds and superstructures, and more importantly on how the symmetry of the molecule influences the 2D crystal. [1] A. Idelson, C. Sterzenbach, S.-S. Jester, C. Tschierske, U. Baumeister, S. Höger, *J. Am. Chem. Soc.* **2017**, *139*, 4429-4434. [2] R. May, S.-S. Jester, S. Höger, *J. Am. Chem. Soc.* **2014**, *136*, 16732-16635. [3] S.-S. Jester, V. Aggarwal, D. Kalle, *Beilstein J. Org. Chem.* **2014**, *10*, 2783-2788.

O 5.10 Mon 12:45 H15

Probing the Potential Landscape of Rotating Co(II)-5,15-diphenylporphyrin on CoO (111) Films — •FEIFEI XIANG and M. ALEXANDER SCHNEIDER — Solid State Physics, Friedrich-Alexander-University Erlangen-Nürnberg, Erlangen, Germany

The adsorption of Co(II)-5,15-diphenylporphyrin (Co-DPP) on CoO (111) films of different thicknesses grown epitaxially on Ir (100) is studied by low-temperature scanning tunneling microscopy (STM) operated at 77 K. Unlike non-metalated DPP (2H-DPP), Co-DPP is observed to rotate around its metal center on CoO (111) films exceeding 1BL thickness at 77 K. By lateral manipulation, the rotation can be switched 'on' and 'off' by moving the rotating molecule to adjacent molecules. The rotating molecule appears in STM as a height modulated round feature, the modulation is attributed to the lifetime of a certain molecular orientation and reflects the local potential landscape.[1] We observe that the modulation patterns of Co-DPP vary with CoO film thickness from 2BL to 11BL. Especially the appearance of a 90° degeneracy of the potential landscape is unexpected in view of the hexagonal surface symmetry of films thicker than 2BL.

Reference

[1] Gao, L.; et al. *Phys. Rev. Lett.* 2008, 101 (19), 197209.