O 92: Nanostructures at Surfaces II

Time: Thursday 15:00–17:45 Location: MA 042

O 92.1 Thu 15:00 MA 042

Shape control in 2D molecular nanosheets by tuning anisotropic intermolecular interactions and assembly kinetics — •Maximilian Dreher[1], Pierre Dombrowski[1], Matthias Tripp[2], Niels Münster[2], Ulrich Koert[2], and Gregor Witte[1] — [1]Philipps-University of Marburg, Physics Department — [2]Philipps-University of Marburg, Chemistry Department

The fabrication of organic nanostructures is hardly applicable by traditional lithographic pattering techniques due to the limited stability of molecular materials. In this study, we present a methodology for achieving controlled mesoscopic shapes in 2D molecular nanosheets through kinetic controlled self-organization. Using van-der-Waals bound molecules, we demonstrate precise control over the shape of nanosheets without modification of their intrinsic molecular packing. Our study focuses on anisotropic attractive Coulomb forces between partially fluorinated pentacenes, evaluating their role in promoting the growth of distinctly elongated nanosheets. Notably, we observe anisotropic elongation between nanosheets grown directly and those fabricated through partial desorption of a complete molecular monolayer. Monte Carlo simulations reveal that lateral intermolecular interactions predominantly drive the different kinetics of nanosheet growth and desorption. By comparing the behavior of differently fluorinated molecules experimentally and computationally, we identify design rules for molecules for effective shaping of organic nanostructures.[1]

[1] M. Dreher et al., Nat Commun (2023), 14, 1554

O 92.2 Thu 15:15 MA 042

Fe-coordinated PcZn(OH)$_8$ Frameworks on Ag(111) by Electrospray-controlled Ion Beam Deposition — •Pengfei Zhao[1], Wei Ran[1], Andreas Walz[1], Annette Hüttig[1], Hartmut Schlichting[1], Renhao Dong[2], Xinliang Feng[2], Anthoula C. Papageorgiou[1,3], Joachim Reichert[1], and Johannes V. Barth[1] — [1]Technical University of Munich, Germany — [2]Dresden University of Technology, Germany — [3]National and Kapodistrian University of Athens, Greece

Molecular engineering of two-dimensional metal-organic frameworks (2D-MOFs) has garnered significant interest for their structural and functional tunability.[1] However, challenges persist in preparing model systems suitable for investigations at the sub-nanometer scale in a well-defined environment. Here, we present a versatile approach to fabricate 2D-MOFs from an un-sublimable metal-phthalocyanine complex (PcZn(OH)$_8$) via electrospray-controlled ion beam deposition (ESCIBD) on a coinage metal surface.[2] By scanning tunneling microscopy, we find that upon adsorption on Ag(111), PcZn(OH)$_8$ features close-packed molecular assemblies stabilized by lateral intermolecular interactions. After dosing Fe and annealing at 423 K, PcZn(OH)$_8$ exhibits Fe-coordinated 2D-MOFs. These results confirm that ESCIBD can expand the on-surface synthesis of MOF-based materials to thermolabile, highly functionalized organic compounds.

Reference

[1] H. Zhong, et al., Nat Commun, 2020, 11, 1409.

[2] A. Walz, et al., Anal Chem, 2022, 94, 7767-7778.

O 92.3 Thu 15:30 MA 042

2D Metal-organic frameworks on the topological insulator Bi_2Se_3(0001) surface — •Matthias Blatnik[1], Anna Kurowská[1], Pavel Procházka[1], and Jan Čechal[1,2] — [1]CEITEC, Brno University of Technology, Brno, CZ — [2]IPE, Brno University of Technology, Brno, CZ

Topological insulators (TI) and other exotic quantum matter have recently drawn much attention due to their fascinating electronic properties. 3D TIs show strong spin-orbit splitting and time-reversal symmetry (TRS) leading to topologically protected surface states with linear, Dirac-like dispersion. Heterostructures of TIs with other materials are highly interesting candidate structures for a variety of applications in new quantum devices and thus of considerable interest for quantum computing, but also optoelectronics or spintronics. Periodic arrays of ferromagnetically coupled transition metal (TM) atoms on the surface of a TI are predicted to spontaneously break TRS and induce a band gap opening at zero magnetic field (i.e., a quantum anomalous Hall effect, QAHE). A 2D metal-organic framework (MOF) of spin-coupled TM atoms ordered by the right organic linkers could be such a candidate. Here, we report on the self-assembly of dicyanoanthracene (DCA) molecules on the topological insulator Bi_2Se_3(0001) surface as a first step, and then the first-time realized 2D Fe-DCA MOFs on the same surface. We apply a variety of surface science techniques (e.g. LEEM, STM, LEED) to investigate and characterize the formation of molecular islands from small to monolayer coverages and study the chemical environment and electronic properties by XPS and ARPES.

O 92.4 Thu 15:45 MA 042

Hot electron lifetime of confined image potential state in a metal-coordinated organic porous network — •Martin Mitkov, Lukas Kau, Ralf Hemm, Martin Anstett, Lu Lyu, Martin Aeschlimann, and Benjamin Stadtmüller — University of Kaiserslautern-Landau and Research Center OPTIMAS, Erwin-Schrödinger Str. 46, 67663 Kaiserslautern, Germany

Two-dimensional metal-organic porous networks (2DMOPNs) on noble metal surfaces are highly ordered quantum boxes for confining surface state electrons. For a long time, this approach has mainly been used for the confinement of surface electrons in Shockley-type surface states and has only recently been explored for excited electrons at surfaces[1] , i.e., image potential state (IPS) electrons. In this contribution, we focus on the hot electron dynamics of quantum confinement IPS electrons in a 2D porous network. As a model system, we study the Cu-coordinated T4PT network on the Cu(111) surface for which the quantum confinement leads to a substantial increase in the effective band mass of the IPS electrons[1]. We use time-resolved two-photon photoemission spectroscopy to quantify the fs timescale hot electron dynamics and quasi-particle lifetimes of the confined electrons in the flat IPS bands. Our findings provide insight into the role of the quantum confinement for the hot electron dynamics in the 2DMOPNs.

[1] Lyu, Lu, et al. arXiv preprint arXiv:2307.06814 (2023).

O 92.5 Thu 16:00 MA 042

On-surface Synthesis of Tunnable Dinuclear Organometallic Networks — •Wenchao Zhao, Nan Cao, Mathias O. Senge, Ethem Akturk, Johannes V. Barth, and Biao Yang — Physics Department E20, School of Natural Sciences, Technical University of Munich, 85748 Garching, Germany

Engineering organometallic networks (OMNs) obtains great efforts due to their potential applications in catalysis, optoelectronic devices etc[1]. Dinuclear metal complexes have multifunctional properties with their tunable structure and hence various applications in the field of OLEDs, chemosensors and smart materials[2]. The relatively complex structure makes it difficult to form thin films for advanced devices application. Therefore, on-surface synthesis of dinuclear organometallic networks serves as a powerful strategy to directly obtain the thin functional layers. Herein, with a designed bi-component precursor and O2-mediated treatment, we manage to construct ordered Ag-Ag dinuclear OMNs containing C-Ag-N bridging linkers. Moreover, it is feasible to tune the the thermal stability and electronic property by replacing the dinuclear metal centers via post metal-exchange method, transferring to Cu-Cu dinuclear with C-Cu-N linkages. This advanced strategy will greatly expand the diversified synthesis and application of dinuclear organometallic supramolecular materials. Reference. 1. D. Ecija et al., Acc. Chem. Res. 2018, 51, 365-375. 2. J. Lv et al., Nature 2023, 622, 754-760.

O 92.6 Thu 16:15 MA 042

Tailoring the ferromagnetic surface potential landscape by a templating two-dimensional metal-organic porous network — •Lu Lyu, Martin Anstett, Ka Man Yu, Azadeh Kadkhodazadeh, Martin Aeschlimann, and Benjamin Stadtmüller — Department of Physics and Research Center OPTIMAS, Rheinland-Pfälzische Technische Universität Kaiserslautern-Landau, Erwin-Schrödinger-Straße 46, 67663 Kaiserslautern, Germany.

Two-dimensional metal-organic porous networks (2D-MOPNs) have emerged as versatile nanoarchitectures for tailoring surface electronic and magnetic properties on noble metals. In this context, we demonstrate the manipulation of the potential landscape of a ferromagnetic surface using a 2D-MOPN structure. As a model surface, we use ultrathin cobalt (Co) films grown on Au(111) which exhibit well-ordered triangular dislocation loops. On this ferromagnetic surface, 2,4,6-tris(4-

pyridyl)-1,3,5triazine (T4PT) molecules can be coordinated with the surface Co atoms, forming a large-scale Co-T4PT porous network. The periodicity of the network acts as a template for the ferromagnetic surface potential and guides the subsequent growth of isolated C60 molecules on the network. For larger submonolayer coverage, the structure of the molecular film is further influenced by the intermolecular interactions between C60 molecules. Our findings underline the potential of 2D-MOPN to template the electronic and spin properties of molecular films on magnetic surfaces.

O 92.7 Thu 16:30 MA 042

Isomorphism of Supramolecular vs. Covalent Binding Motifs in Molecules Forming Two-Dimensional Nanopatterns — •David Ari Hofmeister, Lucas Rothe, Sigurd Höger, and Stefan-Sven Jester — Kekulé-Institut für Organische Chemie und Biochemie, Rheinische Friedrich-Wilhelms-Universität Bonn, Gerhard-Domagk-Str. 1, 53121 Bonn, Germany

The isomorphic packing of different molecules is an established concept in crystallography. Established for three-dimensional (3D) crystals, the concept has recently been extended to two-dimensional (2D) supramolecular patterns of organic molecules on a solid surface, such as highly-oriented pyrolytic graphite (HOPG). The formation of a physisorbed 2D nanopattern is driven by noncovalent interactions. Thereby, different types of interactions (*e.g.* hydrogen bonds and van der Waals interactions) determine the packing, while the balance of interactions is crucial for 2D self-assembly. Here, we substitute a noncovalent interaction motif (*i.e.* the hydrogen bond interaction between two carboxylic acids, R-COOH) with a covalent linkage (a butadiynylene unit). N molecules with COOH groups at opposite ends and an n-mer (in which $n-1$ R-COOH...HOOC-R units are substituted by a butadiynylene unit) pack isomorphously. *In situ* scanning tunneling microscopy at the 1,2,4-trichlorobenzene/HOPG interface provides a submolecularly resolved insight into the nanopatterns formed.

O 92.8 Thu 16:45 MA 042

Dimensional reconstruction of nanoscale grating profile in hybrid approach — •Leonhard Merlin Lohr, Richard Ciesielski, Vinh-Binh Truong, Frank Scholze, and Victor Soltwisch — Physikalisch-Technische Bundesanstalt (PTB), Abbestraße 2-12, 10587 Berlin, Germany

Quality assessment of nanoscale test structures in the semiconductor industry is crucial for the fabrication of devices, such as advanced transistors. The shape of test structures, like nanoscale line gratings, needs to be described with sub-nanometer accuracy. A fast and non-destructive characterization technique is scatterometry, which uses short-wavelength radiation to resolve features of the nanoscale grating. Synchrotron radiation, with its high beam quality probing the structured surface, can be employed to develop the characterization method. A nanoscale grating can be characterized through both soft X-ray scattering and fluorescence. The soft X-ray standing wave field at the structure profile from radiation-surface interaction can be solved using a finite element Maxwell solver and Markov chain Monte Carlo sampling to derive the grating's shape, including uncertainties.

This method is suitable for investigating the potential to enhance reconstruction accuracy by combining complementary measurements in a hybrid measurement scheme. This is illustrated through measurements conducted with a recently presented experimental scattering chamber [1].

[1] R. Ciesielski, L. M. Lohr, A. Fernández Herrero, et al., Rev. Sci. Instrum. 1 Jan 2023; 94 (1): 013904.

O 92.9 Thu 17:00 MA 042

Supramolecular nanopatterns of caltrop-shaped molecular platforms on graphite — •Jakob Gabriel, David Ari Hofmeister, Georgiy Poluektov, Tristan Johannes Keller, Sigurd Höger, and Stefan-Sven Jester — Kekulé-Institut für Organische Chemie und Biochemie, Universität Bonn, Gerhard-Domagk-Str. 1, 53121 Bonn, Germany

Two-dimensional supramolecular nanopatterns of arylene-alkynylenes carrying long alkyl/alkoxy side chains are investigated at the solid/liquid interface on highly oriented pyrolytic graphite (HOPG). Scanning tunneling microscopy provides a submolecularly resolved insight into the nanopatterns formed. In many cases, the exact interdigitation motifs of the side chains are clearly resolved. We have recently reported on molecular spoked wheel architectures with intraannular pillars carrying large entities, such as a perylene monoimide or a fullerene unit, pointing into the volume phase.[1] Here, we focus on investigating a caltrop-shaped tetraphenylmethane derivative with three ”foot” units (instead of a ring-shaped platform). Each of the ”feet” carries two pairs of $OC_{16}H_{33}$ side chains. We evaluate the abundance of different polymorphs that form, when different concentrations in the supernatant liquid phase as well as different solvents are used (1,2,4-trichlorobenzene and 1-phenyloctane).

[1] G. Poluektov, T. J. Keller, A. Jochemich, A. Krönert, U. Müller, S. Spicher, S. Grimme, S.-S. Jester, S. Höger *Angew. Chem. Int. Ed.* **2021**, *60*, 27264.

O 92.10 Thu 17:15 MA 042

Revisiting the realization of artificial graphene by fullerenes on gold and copper surfaces — •Dmitry Marchenko[1], Maxim Krivenkov[1], Maryam Sajedi[1], Alexander Fedorov[1,2], Jaime Sánchez-Barriga[1], Oliver Clark[1], Emile Rienks[1], Oliver Rader[1], and Andrei Varykhalov[1] — [1]Helmholtz-Zentrum Berlin für Materialien und Energie — [2]IFW Dresden

There has been significant progress in the creation of artificial graphene based on molecular networks. For a layer of C60 molecules on Au(111) and Cu(111) surfaces, graphene-like Dirac cones were reported by angle-resolved photoelectron spectroscopy (ARPES). The explanation given is based on a hexagonal network of hollow sites in the 2D surface electron gas, due to the expulsion potential of adsorbed molecules, with the corresponding formation of an electronic honeycomb structure.

Using ARPES and DFT methods we demonstrate [1,2] that the observed bands are neither Dirac cones nor hybridization states. They are formed by final state photoelectron diffraction on a regularly arranged C60 molecular layer. This effect creates a highly coherent pattern of replicated bands, which mimics Dirac cones.

In addition, we discuss in detail the nature of well-known steeply dispersing states in the Au(111) and Cu(111) electronic structure. Traditionally these states are believed to be bulk sp-bands, but we demonstrate that they are a manifold of 2D surface resonance bands leaking into the bulk.

[1] M. Krivenkov et. al., Nanoscale 14, 9124 (2022).

[2] D. Marchenko et. al., Phys. Rev. B 108, 115155 (2023).

O 92.11 Thu 17:30 MA 042

Supramolecular nanopatterns of pentagonal arylene-alkynylenes on graphite — •Israa Abushawish, Vanessa Bobbe, Christian Krewer, Anna Krönert, Georgiy Poluektov, Kristin Gratzfeld, Sigurd Höger, and Stefan-S. Jester — Kekulé-Institut für Organische Chemie und Biochemie, Bonn, Germany

The physisorption of organic molecules at solid surfaces is an effective way to produce highly ordered two-dimensional (2D) nanoscale functional arrays. Shape-persistent arylene- alkynylenes with flexible alkyl/alkoxy substituents decorate the solid/liquid interface of highly oriented pyrolytic graphite (HOPG) and a solution of the compound of interest in 1,2,4- trichlorobenzene (TCB). The so-formed nanopatterns are imaged *in situ* by scanning tunneling microscopy (STM, with the tip immersed into the solution), providing submolecularly resolved insights into the nanopatterns formed. Recently, a series of macrocycles with 3- to 6-fold symmetry has led to the concept of molecular polygons [1,2]. Here, we report on the influence of symmetry, substitution patterns, and the influence of different corner units (i.e. carbazole, dibenzofurane, and dithiophene [1]) on the exact shapes of the molecular pentagons and their different supramolecular packings.

References: [1] S.-S. Jester, E. Sigmund, S. Hoeger, *J. Am. Chem. Soc* 2011, 133, 29, 11062.

[2] P. Wilhelm, J. Vogelsang, G. Poluektov, N. Schönfelder, T. J. Keller, S.-S. Jester, S. Höger, J. M. Lupton, *Angew. Chem. Int. Ed* . **2017**, *56*, 1234.