O 8: Focus Session Molecular Nanostructures on Surfaces: On-Surface Synthesis and Single-Molecule Manipulation I

This focus session aims to discuss recent advances in the on-surface synthesis, manipulation, characterization, and understanding of complex molecular architectures on surfaces. The interest in surface-confined molecular nanostructures emerges from their prospective applications in nanoscale (opto-) electronics, spintronics, solar cells, energy storage devices, and other fields. The bottom-up fabrication of surface-supported nanostructures can be based on molecular self-assembly utilizing non-covalent intermolecular interactions, covalent on-surface synthesis, or the direct manipulation of molecules. Molecular self-assembly usually leads to highly ordered nanostructures, controlled by non-covalent interactions, adsorbate-substrate interactions, as well as thermodynamic and kinetic factors. On-surface synthesis by covalent coupling of reactive precursors adsorbed on metallic, semiconducting, or even insulating surfaces has emerged as a powerful method that has opened new possibilities in exploring new routes towards the synthesis of complex low-dimensional nanostructures with unprecedented material properties, often via novel chemical reactions not available in conventional organic chemistry. Finally, the direct manipulation of molecules with the tip of a scanning probe microscope allows for unprecedented chemical transformations or structural modifications, as envisioned by the pioneers of nanotechnology. This focus session is intended to provide a platform for addressing current trends in these closely linked fields from various perspectives in experiment and theory.

Organized by
Sabine Wenzel (University of Marburg) and Christian Wagner (Forschungszentrum Jülich)

Time: Monday 10:30–13:00 Location: H24

Invited Talk O 8.1 Mon 10:30 H24

Chiral reactions at surfaces elucidated by machine learning and enhanced sampling — Raymond Amador[1], Enrico Trizio[2], Peilin Kang[2], Umberto Raucci[2], Hannah Bertschi[1], Marcella Iannuzzi[3], Jacob Wright[1], Roland Widmer[1], Oliver Gröning[1], Michele Parrinello[2], and •Daniele Passerone[1] — [1]Empa, Swiss Federal Laboratories for Materials Science and Technology, Dübendorf, Switzerland — [2]Italian Institute of Technology, Genova, Italy — [3]Department of Chemistry, University of Zurich, Switzerland

Experiments performed at the surface of the chiral intermetallic compound PdGa unleash a fascinating surface chemistry phenomenology including regioselectivity and enantioselectivity, in which the energetics is dominated by mid-range dispersive molecular interactions with the substrate. The corresponding modelling of chiral and prochiral adsorption and reactions requires both a high level of electronic structure theory and an appropriate statistical sampling of the reactants, transition state and products ensemble. We show that machine learning potentials based on DFT molecular dynamics trajectories and recently introduced enhanced sampling techniques allow to describe both the thermodynamics and the kinetics of reactions investigated in the laboratories next-door, such as an Orito-like reaction catalysed by PdGa. Moreover, we study a chirality switching of a bianthracene molecule by applying a method introduced by some of us, based on the committor function and the variational principle that it obeys: its minimum uses a self-consistent procedure that starts from information limited to the initial and final states and reveals the transition state ensemble.

O 8.2 Mon 11:00 H24

On-surface molecular recognition driven by chalcogen bonding — •Luca Camilli — University of Rome Tor Vergata

The manipulation of organic architectures on surfaces through supramolecular interactions has been achieved by using, for example, H- and halogen-bonding. Chalcogen bonding interactions (ChBIs), which belongs to the same category, have not. The interest in ChBIs relies on its orbital mixing nature that provides semiconducting properties to the assemblies.[1] Here, we combine scanning tunnelling microscopy measurements and quantum chemistry calculations to present the first example of ChBI-driven molecular self-assembly on metal surfaces.[2] We show that pyrene-based modules bearing chalcogenazole pyridine moieties undergo self-assembly into dimers through double Ch***N interactions on Au(111) and Ag(110). Synchrotron-based spectroscopy techniques are used to gain more insights into the chemistry of the ChBI and to reveal its fingerprint [unpublished data]. Finally, experimental scanning tunnelling spectroscopy and its simulations based on the framework of density functional theory are used to investigate the electronic properties of the self-assembled systems [unpublished data]. This study sheds light on a promising avenue for future research in the bottom-up engineering of two-dimensional monolayered supramolecular chalcogenide-type materials, as we delve into the novel role of ChBIs in surface-based molecular recognition.

References 1. D. Romito et al. Angew. Chem. Int. Ed. 2022, 61 (38), e202202137. 2. L. Camilli, et al. JACS Au 4, 2115 (2024)

O 8.3 Mon 11:15 H24

Self-assembly, electronic structure, and switching of norbornadiene derivative photoswitches — •Shreya Garg[1], Vishakya Jayalatharachchi[1], Pedro Ferreira[2], Roberto Robles[3], Sajjan Mohammad[1], Shivani Singh[1], Nicolás Lorente[3,4], Kasper Moth-Poulsen[2], Meike Stöhr[1,5], and Sabine Maier[1] — [1]Department of Physics, Friedrich Alexander University Erlangen-Nürnberg, Germany — [2]Polytechnic University of Catalonia, Catalonia, Spain — [3]Centro de Física de Materiales CFM/MPC (CSIC-UPV/EHU), Donostia-San Sebastian, Spain — [4]Donostia International Physics Center (DIPC), San Sebastian — [5]University of Applied Sciences of the Grisons, Switzerland

Molecular photoswitches such as norbornadiene (NBD) derivatives are promising energy storage compounds due to their ability to switch to the metastable quadricyclane (QC) isomer with long half-lives and high-energy storage density. However, the NBD/QC derivative photoswitches remain largely unexplored on the surface. Here, we discuss the self-assembly, electronic structure, and switching of carboxylic acid-functionalized NBD derivative on the Au(111) surface using scanning tunneling microscopy complemented by density functional theory calculations. To explore the impact of the molecule-surface interactions, we also studied them on graphene, which acts as a decoupling layer. We observed distinct hydrogen-bonding motifs between the NBD derivatives on the two surfaces. Our study highlights differences in the electronic properties between the Au(111) and graphene surface, providing insights into optimizing their switching performance on surfaces.

O 8.4 Mon 11:30 H24

Kinetics of the on-surface reactions of 3,3"-dibromo-p-terphenyl on Cu(111): Cis-trans isomerization as rate limiting step towards the final configurations — •Mohit Jain[1], Tamam Bohamud[1], Daniel Kohrs[2], Nathaniel Ukah[2], Hermann A. Wegner[2], and Michael Dürr[1] — [1]Institut für Angewandte Physik and Zentrum für Materialforschung, Justus-Liebig-Universität Giessen, Germany — [2]Institut für Organische Chemie and Zentrum für Materialforschung, Justus-Liebig-Universität Giessen, Germany

The kinetics of the on-surface synthesis reactions of 3,3"-dibromo-p-terphenyl were investigated at fixed surface temperature of 300 K. The initially adsorbed molecules linked through C-Cu-C bonds were found in configurations consisting of long, chain-like and few shorter ring-like structures. With the progression of the reaction through time at

300 K, the configurations showed a shift from long chains and closed structures to 3-molecule ring structures. These structures then slowly aligned to form surface-wide phases of 3-molecule closed-ring structures.

The lateral surface mobility of the molecules was observed to be high at 300 K along with the frequent cleavage and re-formation of the C-Cu-C bond; nevertheless the actual transformation of chain structures towards complete ring structures was detected at a much longer timescale. By quantitative analysis, the trans-to-cis isomerization of the molecules which is necessary for closed-ring formation, was found to be the rate limiting step. To further consolidate the results, experiments with different substitution patterns of the p-terphenyl molecules were performed.

O 8.5 Mon 11:45 H24

Stability and Reactivity of Fe-DCA 2D Metal-Organic Framework on Graphene — •Zdeněk Jakub[1], Dominik Hrůza[1], Taduáš Lesovský[1], Ayesha Jabeen[1], Jakub Planer[1], Pavel Procházka[1], and Jan Čechal[1,2] — [1]CEITEC - Central European Institute of Technology, Brno University of Technology, Purkyňova 123, Brno 61200, Czechia — [2]Institute of Physical Engineering, Faculty of Mechanical Engineering, Brno University of Technology, Technická 2896/2, Brno 61200, Czechia

2D Metal-Organic Frameworks (2D MOFs) are promising materials for applications in catalysis, sensing or spintronics. 2D MOFs based on 9,10-dicyanoanthracene (DCA) linker molecules are particularly intriguing due to their recently demonstrated magnetic and topological properties. Here, we study the reactivity of Fe-DCA supported on a weakly-interacting substrate, graphene/Ir(111). Using Scanning Tunneling Microscopy (STM), X-Ray Photoemission Spectroscopy (XPS) and Low-Energy Electron Microscopy/Diffraction (LEEM/LEED) we test how the Fe-DCA responds to exposure to CO, O_2, and thermal annealing. Our data indicate that CO readily adsorbs at room temperature, and the 2D MOF remains stable. In contrast, adsorption of O_2 causes structural collapse of the 2D MOF, leaching the Fe cations from the Fe-DCA islands and leaving patches of self-assembled DCA on the surface. Thermally, the Fe-DCA structure decomposes upon annealing above 100 °C. Overall, our work addresses the limits of thermal and chemical stability of metal-DCA systems; such knowledge is relevant for any potential application of these materials.

O 8.6 Mon 12:00 H24

Tuning the properties of 2D Metal-Organic Frameworks by doping of the support — •Ayesha Jabeen[1], Zdeněk Jakub[1], Dominik Hrůza[1], Lenka Černá[1], Pavel Procházka[1], Jakub Planer[1], and Jan Čechal[1,2] — [1]CEITEC-Central European Institute of Technology, Brno University of Technology, Purkyňova 123, Brno 61200, Czech Republic — [2]Institute of Physical Engineering, Faculty of Mechanical Engineering, Brno University of Technology, Technická 2896/2, Brno 61200,Czech Republic

2D metal-organic frameworks (MOFs) are extensively studied due to their tailorable properties, which make them promising for applications in catalysis, energy storage and sensing. Here, we show how the properties of 2D MOFs can be further tuned by varying the energy-level alignment with the supporting surface. We demonstrate this on the case of Ni-TCNQ 2D MOF, that we synthesized atop graphene/Ir(111) with different doping levels. The graphene doping is achieved by intercalation of heteroatoms at the graphene/Ir(111) interface; namely oxygen (for p-doping) and dysprosium (for n-doping). The changes in the support*s Fermi level position are clearly identified by photoemission techniques (XPS/UPS/ARPES). The Ni-TCNQ 2D MOFs supported on differently doped graphene show distinct properties, as evidenced by STM, XPS and LEEM/LEED. Most notably, XPS suggests that the charge state of the embedded Ni atoms can be controlled, as we observe two distinct components of Ni core levels, whose ratio depends on the support′s doping level. These findings highlight the potential of support doping for tailoring the properties of designer 2D MOFs.

O 8.7 Mon 12:15 H24

Theoretical Investigation of Dibromopyrene and Iodotriphenylene on Sodium Chloride Coated Copper Substrate — •Florian Pfeiffer[1], Julian Ernst[1], André Schirmeisen[2], Daniel Ebeling[2], and Simone Sanna[1] — [1]Institute for Theoretical Physics, Justus Liebig University Giessen, Germany — [2]Institute for Applied Physics, Justus Liebig University Giessen, Germany

Organic 2D materials are of great interest for various applications in molecular electronics. Increasingly sophisticated methods of on-surface manipulation via probe tips extend the scope of possible structure modifications to tune the (electronic) properties of such nanostructures.

Halogenated organic precursors such as DBP and IT are the building blocks for the assembly of more complex structures. A sodium chloride bilayer helps to electronically decouple the metallic Cu(111) substrate from adsorbates, increasing mobility and thus simplifying manipulation.

The Vienna Ab initio Simulation Package [1] implementation of density functional theory was used to calculate potential energy surfaces and nudged elastic bands for modelling adsorption behaviour and diffusion pathways, respectively. Comparability with experimental results [2] was achieved by simulation of scanning tunneling and atomic force microscopy using the Probe-Particle Model [3].

[1] G. Kresse and J. Hafner, Phys. Rev. B 47, 558 (1993)
[2] Q. Zhong et al., Nat. Chem. 13, 1133 (2021)
[3] P. Hapala et al., Phys. Rev. B 90, 085421 (2014)

O 8.8 Mon 12:30 H24

On-Surface Design of Highly-Ordered Two-Dimensional Networks Stabilized by Nonmetal Atoms — •Alisson Ceccatto[1,3], Gustavo Campi[2], Vanessa Carreño[1], Eidsa Ferreira[1], Natalie J. Waleska-Wellnhofer[3], Eva Marie Freiberger[3], Simon Jaekel[3], Duncan John Mowbray[2], Christian Papp[3,4], Hans-Peter Steinrück[3], and Abner de Siervo[1] — [1]Geb Wataghin Physics Institute - University of Campinas - Campinas/Brazil — [2]School of Physical Sciences and Nanotechnology, Yachay Tech University, 100119 Urcuquí, Ecuador — [3]Lehrstuhl für Physikalische Chemie II, Friedrich-Alexander-Universität Erlangen-Nürnberg, Egerlandstr. 3, 91058 Erlangen, Germany — [4]Angewandte Physikalische Chemie, FU Berlin, Arnimallee 22, 14195 Berlin, Germany

Supramolecular nanoarchitectures have been widely explored to precisely design low-dimensional materials at atomic and molecular levels. Herein, by combining STM measurements and DFT calculations, we report the 2D self-assembled of 1,3,5-tris[4-(pyridin-4-yl)-[1,1-biphenyl])benzene (TPyPPB) molecules on Ag(111) in the presence of Cl adatoms. The adsorption of the TPyPPB molecules on the clean Ag(111) surface forms a porous SAM stabilized by hydrogen bonds. Such packing can be explored as a host-guest material for atom/molecular confinement. However, in the presence of Cl adatoms, the molecular arrangement changes dramatically. The molecular assembly changes its geometry, forming a non-porous SAM stabilized by unconventional H–Cl–H bonds.

O 8.9 Mon 12:45 H24

On-surface synthesis of drone-shaped oligomers via carbenes — •Yunjun Cao[1], Joel Mieres-Perez[2], Julien Frederic Rowen[3], Akshay Hemant Raut[3], Paul Schweer[1], Wolfram Sander[3], Elsa Sanchez-Garcia[2], and Karina Morgenstern[1] — [1]Physical Chemistry I, Ruhr-Universität Bochum, D-44801 Bochum, Germany — [2]Lehrstuhl Physikalische Chemie I, NC 5/72, Ruhr-Universität Bochum, 44801, Bochum — [3]Organic Chemistry II, Ruhr-Universität Bochum, D-44801 Bochum, Germany

The development of on-surface synthesis strategies opens opportunities to fabricate sophisticated nanostructures with tailored geometries, symmetries, and other properties. Here, we demonstrate that carbenes can be used as building blocks for fabricating highly branched oligomers with different symmetries on a Ag(111) surface. We synthesize highly symmetric drone-shaped oligomers, which are formed via C=C coupling of two carbenes to create a core, followed by C-H activation of the core with additional carbenes to create branches. Less symmetric drone-shaped oligomers are formed through the cyclodehydrogenation of the highly symmetric oligomers. The products are investigated by scanning tunneling microscopy and supported by ab initio theoretical modeling.