O 62: Focus Session Molecular Nanostructures on Surfaces: On-Surface Synthesis and Single-Molecule Manipulation III

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: Wednesday 10:30–13:00 Location: H24

O 62.1 Wed 10:30 H24

Selective On-Surface Synthesis of Isokekulene Facilitated by Strong Molecule-Substrate Interaction — Qitang Fan[1], Alexander Reichmann[2], Zilin Ruan[1], Faming Kang[1], Tim Naumann[1], Simon Werner[1], Olaf Kleykamp[1], Jose Martinez[3], Felix Lüpke[3], François C. Bocquet[3], Christian Kumpf[3], Serguei Soubatch[3], Jörg Sundermeyer[1], Peter Puschnig[2], F. Stefan Tautz[3], J. Michael Gottfried[1], and •Sabine Wenzel[1,3] — [1]Fachbereich Chemie, Philipps-Universität Marburg — [2]Institute of Physics, University of Graz — [3]Peter Grünberg Institut (PGI-3), Forschungszentrum Jülich

The role of different facets of metal nanoparticles in steering reaction pathways is crucial for the design of heterogeneous catalysts with superior selectivity. Transition-metal-catalyzed C-H bond activation is widely used for the synthesis of different chemicals. Here, we report orthogonal selectivity in intramolecular cyclodehydrogenation of a nonplanar cyclic precursor steered by different facets of a copper single crystal. On Cu(110), the previously unknown cycloarene isokekulene is formed with a high selectivity of 92 %, while reaction on Cu(111) is known to result in kekulene (> 99 %). Combining scanning tunneling microscopy with CO-functionalized tips and density functional theory, we identify two adsorption geometries of the precursor which react to the respective products. The isokekulene molecule appears in two nonplanar adsorption configurations and shows a strong molecule-substrate interaction including charge transfer, which accounts for the more favorable energetics of isokekulene on Cu(110).

O 62.2 Wed 10:45 H24

On-surface synthesis and characterization of long azaacenes — •Zilin Ruan[1], Liping Ye[2], Jakob Schramm[3], Tim Naumann[1], Faming Kang[1], Ralf Tonner-Zech[3], Michael Mastalerz[2], and J. Michael Gottfried[1] — [1]Department of Chemistry, Philipps-Universität Marburg, 35037 Marburg, Germany — [2]2Organisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg, 69120 Heidelberg, Germany — [3]Wilhelm Ostwald Institute of Physical and Theoretical Chemistry, Universität Leipzig, 04103 Leipzig, Germany

Introducing electronegative nitrogen into the backbone of acenes yields azaacenes, enabling fine-tuning of the energy alignment of frontier orbitals while enhancing resistance to oxidation, photodegradation, and dimerization. Here, we demonstrate the on-surface synthesis of tetraazanonacene and hexaazatridecacene, the latter being the longest azaacene known to date and here reported for the first time via atom-manipulation-induced dissociation of a trietheno-bridged precursor on a Au(111) surface in UHV. The geometric and electronic structures of the generated azaacenes were investigated by combined scanning tunneling microscopy/spectroscopy and non-contact atomic force microscopy. For tetraazanonacene, we observed an increase of the frontier orbital gap compared to pristine nonacene, attributed to a more pronounced downshift of occupied states. Meanwhile, hexaazanonacene exhibited an open-shell singlet ground state with a singlet-triplet gap of 110 meV, slightly smaller than that observed for long acenes.

O 62.3 Wed 11:00 H24

On-surface synthesis and characterization of polyynic carbon chains — •Wenze Gao[1,2], Wei Zheng[1], Luye Sun[1], Faming Kang[1], Zheng Zhou[1], and Wei Xu[1] — [1]Interdisciplinary Materials Research Center, School of Materials Science and Engineering, Tongji University, Shanghai, China — [2]Empa-Swiss Federal Laboratories for Materials Science and Technology, Dübendorf, Switzerland

Carbyne, an elusive sp-hybridized linear carbon allotrope, has fascinated chemists and physicists for decades. Due to its high chemical reactivity and extreme instability, carbyne was much less explored in contrast to the sp2-hybridized carbon allotropes such as graphene. Herein, we report the on-surface synthesis of polyynic carbon chains by demetallization of organometallic polyynes on the Au(111) surface; the longest one observed consists of 60 alkyne units (120 carbon atoms). The polyynic structure of carbon chains with alternating triple and single bonds was unambiguously revealed by bond-resolved atomic force microscopy. Moreover, an atomically precise polyyne, C14, was successfully produced via tip-induced dehalogenation and ring-opening of the decachloroanthracene molecule (C14Cl10) on a bilayer NaCl/Au(111) surface at 4.7 K, and a band gap of 5.8 eV was measured by scanning tunnelling spectroscopy, in a good agreement with the theoretical HOMO-LUMO gap (5.48 eV).

O 62.4 Wed 11:15 H24

The odd-number cyclo[13]carbon and its dimer, cyclo[26]carbon — •Florian Albrecht[1], Igor Rončević[2], Yueze Gao[2], Fabian Paschke[1], Alberto Baiardi[3], Ivano Tavernelli[3], Shantanu Mishra[1], Harry L. Anderson[2] und Leo Gross[1] — [1]IBM Research Europe - Zurich — [2]Department of Chemistry, Oxford Univeristy — [3]IBM Quantum, IBM Research Europe - Zurich

Using CO-functionalized tips, we generate the odd-numbered cyclocarbon molecule cyclo[13]carbon (C13) on an ulatra-thin insulating film by applying voltage pulses to a stable precursor molecule. The geometric and electronic properties of C13 were characterized experimentally as well as theoretically, determining the electronic ground state to be an open-shell triplet. In addition to the C13 monomer, we also generated its dimer, cyclo[26]carbon, from two precursor molecules [1].

[1] Albrecht et al., Science 384, 677 (2024)

Invited Talk O 62.5 Wed 11:30 H24

On-Surface Synthesis with Hydrogen Atoms — •Szymon Godlewski — Jagiellonian University, Krakow, Poland

In recent years the on-surface manipulation and chemical reactions created a playground for atomically precise synthesis and development of new atomic and molecular nanostructures. However, the abilities to produce desired systems are limited, among others, by relying on the catalytic role of the substrate in initiating selected reactions. Therefore striving for the generation of desired systems forces the search of new reaction pathways and catalytic transformations.

In this talk I will demonstrate our approach based on the application of hydrogen atoms in the on-surface experiments. First, I will discuss the synthesis of the acene series based on the application of *extra* hydrogen atoms. The application of atomic hydrogen in on-surface transformations will be exemplified by organometallic hybrids and graphene nanoribbons.

While the surface assisted synthesis approach has proven its effectiveness in the precise formation of new organic compounds on metallic surfaces one of the most challenging limitations arises from the dependence on the catalytic activity of the substrate. This makes the direct transfer to the non-metallic surfaces extremely challenging. In this talk I will present our pathway for the synthesis of new molecular compounds on non-metallic surfaces with prospects for circumventing the need to exploit the catalytic role of metallic substrates.

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O 62.6 Wed 12:00 H24

On-Surface Synthesis of Hydrogen-Substituted γ-Graphdiyne with High Efficiency — •Faming Kang[1,3], Wei Zheng[1], Luye Sun[1], Wenze Gao[1], Lina Shang[1], Lifeng Chi[2], and Wei Xu[1] — [1]Interdisciplinary Materials Research Center, School of Materials Science and Engineering, Tongji University, 201804 Shanghai, China — [2]Institute of Functional Nano & Soft Materials (FUNSOM), Jiangsu Key Laboratory for Carbon-Based Functional Materials and Devices, Joint International Research Laboratory of Carbon-Based Functional Materials and Devices, Soochow University, 215123 Suzhou, China — [3]Department of Chemistry, University of Marburg, 35032 Marburg, Germany

Graphyne-family structures, a group of hybrid carbon allotropes with sp- and sp2-hybridized carbon atoms, are expected to have unique features, including a natural direct bandgap, unlike graphene. Here, we developed and synthesized precursors with one and three tribromoethenyl groups. In mild conditions, metal-free dimer and network (HsGDY) products were synthesized in big scale and good quality. The geometric structure of synthesized dimer and network products was accurately characterized by scanning tunneling microscopy and non-contact atomic force microscopy. The electronic structures of produced hydrogen-substituted graphdiyne were studied using DFT calculations. Our research may motivate theoretical and experimental efforts to create more sensitive two-dimensional carbon nanostructures with sp-hybridized carbon atoms.

O 62.7 Wed 12:15 H24

Tip-induced nitrene generation — •Leonard-Alexander Lieske[1], Aaron Oechsle[1], Ilias Gazizullin[2], Matthias Krinninger[3], Igor Rončević[4], Florian Albrecht[1], Leonhard Grill[2], Friedrich Esch[3], and Leo Gross[1] — [1]IBM Research Europe - Zurich, Rueschlikon, Switzerland — [2]Physical Chemistry Department, University of Graz, Graz, Austria — [3]Chair of Physical Chemistry and Catalysis Research Center, Department of Chemistry, TUM School of Natural Sciences, Technical University of Munich, Garching, Germany — [4]Department of Chemistry, University of Manchester, Manchester, United Kingdom

We have successfully generated mono-, di- and trinitreno-*s*-heptazine by tip-induced chemistry from the precursor 2,5,8-triazido-*s*-heptazine[1,2] on bilayer NaCl and on bare Au(111). The precursor's azide groups are cleaved off sequentially in a controlled manner, demonstrating the generation of single molecules with one, two and three nitrene moieties, which are highly reactive.[3] We characterized the mono-, di- and trinitrene species by high-resolution atomic force microscopy with CO functionalized tips[4] and by scanning tunneling microscopy. Broken-symmetry density functional theory and multireference complete active space calculations of inter- and intra-nitrene exchange couplings J and J^* suggest a high-spin ($S = 3$) ground state for trinitreno-*s*-heptazine. [1] D. Miller et al., *J. Am. Chem. Soc.*, 126, 5372 (2004). [2] M. Krinninger et al., *Chem. Mater.*, 35, 6762 (2023). [3] M. Janssen et al., *Science*, 385, 318 (2024). [4] L. Gross et al., *Science*, 325, 1110 (2009).

O 62.8 Wed 12:30 H24

On-Surface Synthesis and Reactivity of Biphenylene Network on Au(788) — •Ye Liu, Yingling Zhang, Zilin Ruan, Tim Naumann, Faming Kang, Ulrich Koert, and J. Michael Gottfried — Department of Chemistry, University of Marburg, 35032 Marburg, Germany

The recently synthesized biphenylene network (BPN), a new sp2-hybridized carbon allotrope comprising four-, six-, and eight-membered rings, significantly differs from graphene in its electronic and chemical properties. Theoretical studies predict that BPN features a multiradical ground state, with its open-shell character predominantly localized at the four-membered rings. However, experimental confirmation of these predictions has been hindered by the limited quality of the material currently available. To address this challenge, we employed Au(788), a surface characterized by narrow terraces, and designed an extended molecular precursor to promote the formation of the desired structure. For comparison, we also investigated inter-polymer dehydrofluorination (HF-zipping) reactions of the precursor on Au(111). Scanning probe microscopy (SPM) analysis revealed that pure BPN fused chains formed on Au(788) exhibit superior structural quality compared to those synthesized on Au(111). These findings provide a solid experimental foundation for probing the theoretically predicted properties of BPN, opening avenues for the further exploration of its distinctive electronic and chemical behavior.

O 62.9 Wed 12:45 H24

Incorporating Nonhexagonal Polygons into Carbon-Based Nanostructures via On-Surface Synthesis — •Dong Han[1], Jakob Schramm[2], Zilin Ruan[1], Tim Naumann[1], Konstantin Y. Amsharov[3], Ralf Tonner-Zech[2], and J. Michael Gottfried[1] — [1]Department of Chemistry, Philipps-Universität Marburg, Marburg, Germany — [2]Faculty of Chemistry and Mineralogy, Wilhelm Ostwald Institute for Physical and Theoretical Chemistry, Universität Leipzig, Leipzig, Germany — [3]Institute of Chemistry, Organic Chemistry, Martin-Luther-Universität Halle-Wittenberg, Halle, Germany

The incorporation of nonhexagonal rings offers a powerful strategy for designing novel carbon-based nanostructures with unique physicochemical properties. Herein, we report the on-surface synthesis of: (1) Quasi-planar, furan-containing cycloparaphenylenes (CPPs): Synthesized via Ullmann coupling and cyclodehydrogenation on Au(111), these CPPs show a decreasing energy gap with increasing size. Orbital confinement at edges and pores is observed, which is associated with the slower wave function decay above the CPP plane. (2) Carbon nanoribbons (CNRs) embedded with nonbenzenoid rings: Zigzag nanoribbons bearing 5-6-7 membered rings and linear nanoribbons containing 4-5-6-8 carbon polygons are formed through the lateral fusion of polymer chains on Au(111). Low-temperature scanning tunneling microscopy/spectroscopy (STM/STS) reveals their geometric and electronic properties, and X-ray photoelectron spectroscopy (XPS) unravels the reaction process.