O 20: Focus Session: Molecular Nanostructures on Surfaces: On-Surface Synthesis and Single-Molecule Manipulation I

Surface-confined molecular nanostructures hold promise for applications in nanoscale (opto-) electronics, spintronics, solar cells, energy storage, and more. The bottom-up fabrication involves molecular self-assembly using non-covalent interactions, covalent on-surface synthesis, or direct molecule manipulation. Self-assembly yields highly ordered nanostructures influenced by non-covalent and adsorbate-substrate interactions, thermodynamics, and kinetics. Covalent on-surface synthesis on metallic, semi-conducting, or insulating surfaces offers new routes for complex low-dimensional nanostructures with unique properties. Direct manipulation with a scanning probe microscope enables unprecedented chemical transformations. The Focus Session provides a platform to discuss current trends in these interconnected fields from diverse experimental and theoretical perspectives. It addresses recent advancements in on-surface synthesis, manipulation, characterization, and comprehension of complex molecular architectures.

Organizer: Michael Gottfried (U Marburg), Sabine Maier (U Erlangen-Nürnberg)

Time: Tuesday 10:30–13:00 Location: HE 101

Topical Talk O 20.1 Tue 10:30 HE 101

Generation and Characterization of Cyclocarbons — Florian Albrecht[1], Igor Roncevic[2], Yueze Gao[2], Fabian Paschke[1], Shantanu Mishra[1], Harry L. Anderson[2], and •Leo Gross[1] — [1]IBM Research Europe - Zurich, Rüschlikon, Switzerland — [2]Oxford University, Oxford, United Kingdom

The family of carbon allotropes was expanded by tip-induced synthesis and on-surface characterization of cyclo[N]carbons, molecular rings composed of N carbon atoms [1-3]. Cyclocarbons possess two orthogonal delocalized pi-systems and can undergo different Jahn-Teller distortions rendering them excellent systems for benchmarking theory [4-6]. Even-N cyclocarbons can be doubly aromatic [1,3] or doubly anti-aromatic [2], and can exhibit polyynic [1,2] or cumulenic [3] structures. Odd-N cyclocarbons [5,7] do not allow a symmetric polyynic structure, might be open-shell systems, and will be discussed in the talk.

References: [1] K. Kaiser et al. Science 365, 1299-1301 (2019). [2] Y. Gao. et al. Nature 623, 977-981 (2023). [3] L. Sun, et al. Nature 623, 972-976 (2023). [4] G. V. Baryshnikov et al. J. Phys. Chem. A 124, 10849-10855 (2020). [5] G. V. Baryshnikov et al. J. Phys. Chem. A 126, 2445-2452 (2022). [6] I. Rončevic et al. (2023) 10.26434/chemrxiv-2023-8kc5t-v2. [7] F. Albrecht et al. (2023) 10.26434/chemrxiv-2023-ddrh7.

O 20.2 Tue 11:00 HE 101

Probing charge redistribution at the interface of self-assembled cyclo-P5 pentamers on Ag(111) — •Remy Pawlak[1], Outhmane Chahib[1], Yulin Yin[2], Jung-Ching Liu[1], Chao Li[1], Thilo Glatzel[1], Feng Ding[2], Qinghong Yuan[3], and Ernst Meyer[1] — [1]Department of Physics, University of Basel, Basel, Switzerland — [2]Chinese Academy of Sciences, Shenzhen, China — [3]East China Normal University, Shanghai, China

Phosphorus pentamer (cyclo-P_5^-) ions are unstable in nature but can be synthesized at the Ag(111) surface. Unlike monolayer black phosphorous, little is known about their electronic properties when in contact with metal electrodes, although this is crucial for future applications. Here we characterize the atomic structure of cyclo-P_5 assembled on Ag(111) using atomic force microscopy with functionalized tips and density functional theory. Combining force and tunneling spectroscopy, we find that a strong charge transfer induces an inward dipole moment at the cyclo-P_5/Ag interface as well as the formation of an interface state. We probe the image potential states by field-effect resonant tunneling 1and quantify the increase of the local change of work function of 0.46 eV at the cyclo-P_5 assembly. Our results suggest that the high-quality of the cyclo-P_5/Ag interface might serve as a prototypical system for electric contacts in phosphorus-based semiconductor devices.

O 20.3 Tue 11:15 HE 101

On-Surface Synthesis and Characterization of Pentadecacene — •Zilin Ruan[1], Tim Naumann[1], Jakob Schramm[2], John B. Bauer[3], Holger F. Bettinger[3], Ralf Tonner-Zech[2], and J. Michael Gottfried[1] — [1]Department of Chemistry, University of Marburg, 35043 Marburg (Germany) — [2]Wilhelm Ostwald Institute of Physical and Theoretical Chemistry, University of Leipzig, 04103 Leipzig (Germany) — [3]Institute for Organic Chemistry, University of Tübingen, 72076 Tübingen (Germany)

Acenes represent a unique class of polycyclic aromatic hydrocarbons that have fascinated chemists and physicists due to their exceptional potential for use in organic electronic applications. Here, we demonstrate the on-surface synthesis of pentadecacene, the longest acene 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 under ultra-high vacuum conditions. The geometric and electronic structures of the generated acene have been investigated by combined scanning tunneling microscopy/spectroscopy and non-contact atomic force microscopy. We observed an antiferromagnetic open-shell ground state electron configuration for pentadecacene from a spin-excitation feature at low bias, giving a singlet-triplet gap of around 124 meV. Alternatively, upon a thermal cracking of the trietheno-bridges at higher temperature, pentadecacene can be also generated and spontaneously forms complex structure with up to 6 gold atoms on Au(111) surface, suggesting a considerable multiradical contribution to its electronic ground state.

O 20.4 Tue 11:30 HE 101

On-Surface Stepwise Double Dehydrogenation for the Formation of an Undecacene Isomer — •Suchetana Sarkar[1], Kwan Ho Au-Yeung[1], Berta Álvarez[2,3], Agustín Cobas[3], Roberto Robles[4], Nicolas Lorente[4,5], Diego Peña[2,3], Dolores Pérez[2,3], and Francesca Moresco[1] — [1]Center for Advancing Electronics Dresden, TU Dresden, 01062 Dresden, Germany — [2]Centro de Investigación en Química Biolóxica e Materiais Moleculares (CiQUS), Universidade de Santiago de Compostela, Santiago de Compostela 15782, Spain — [3]Departamento de Química Orgánica, Universidade de Santiago de Compostela, Santiago de Compostela 15782, Spain — [4]Centro de Física de Materiales CFM/MPC (CSIC-UPV/EHU), 20018 Donostia-San Sebastián, Spain — [5]Donostia International Physics Center, 20018 Donostia-San Sebastián, Spain

We present the on-surface synthesis of an isomer of undecacene bearing two four-membered rings and two para-quinodimethanes. The transformation involves a thermal double deoxygenation followed by on-surface stepwise double dehydrogenation reaction of the methyl groups, locally induced by inelastic tunneling electrons on an Au (111) substrate. The structure and electronic properties of the intermediates and the final product have been investigated at the single molecule level with high spatial resolution, using both low temperature scanning tunneling microscopy/spectroscopy and non-contact atomic force microscopy. The experimental results are supported by density functional theory calculations.

O 20.5 Tue 11:45 HE 101

High-Yield On-Surface Synthesis of Isokekulene Facilitated by Strong Molecule-Substrate Interaction — •Sabine Wenzel[1], Qitang Fan[2], Anja Haags[1], Alexander Reichmann[3], Larissa Egger[3], Hans Kirschner[4], Tim Naumann[2], Simon Werner[2], Tobias Vollgraff[2], Jörg Sundermeyer[2], Jose Martinez[1], Felix Lüpke[1], Xiaosheng Yang[1], Dominik Brandstetter[3], François C. Bocquet[1], Christian Kumpf[1], Georg Koller[3], Alexander Gottwald[3], Mathias Richter[4], Michael Ramsey[3], Peter Puschnig[3], Serguei Soubatch[1], F. Stefan Tautz[1], and J. Michael Gottfried[2] — [1]Peter Grünberg

Institut (PGI-3), Forschungszentrum Jülich — [2]Fachbereich Chemie, Philipps-Universität Marburg — [3]Institute of Physics, University of Graz — [4]Physikalisch-Technische Bundesanstalt (PTB), Berlin

Recent progress in on-surface synthesis has enabled the formation of novel aromatic molecules such as nanographenes, nanoribbons, and cycloarenes. Thereby, the choice of metal crystal and its surface termination can have a strong influence on the selectivity of the synthesis reaction. Here, we report the formation of the novel nonplanar cycloarene isokekulene on Cu(110) and compare it to the planar kekulene which forms on Cu(111) from the same precursor. Combining density functional theory, scanning tunneling microscopy with a CO-functionalized tip, and photoemission orbital tomography, we identify two adsorption configurations of isokekulene and reveal a strong molecule-substrate interaction including charge transfer, which account for the more favorable energetics of isokekulene on Cu(110).

O 20.6 Tue 12:00 HE 101

On-surface Synthesis of Nitrogen-Doped Carbon Nanostructures — •Tim Naumann[1], Zilin Ruan[1], Olaf Kleykamp[1], Alix Kaczmarek[2], Eugen Sharikow[1], Jörg Sundermeyer[1], Doreen Mollenhauer[2], and J. Michael Gottfried[1] — [1]Department of Chemistry, University of Marburg, 35043 Marburg, Germany — [2]Department of Chemistry, University of Giessen, 35392 Giessen, Germany

The electronic and magnetic properties of carbon-based nanomaterials can be tailored by altering the topology, introducing defect sites like vacancies, or doping with heteroatoms. Here, we present an on-surface synthesis route to a variety of nitrogen-containing 0D and 1D carbon nanostructures starting from one single precursor. Annealing 4-([1,1'-biphenyl]-2-yl)-2,6-dibromopyridine on Au(111) leads to Ullmann-coupling of the precursor molecules followed by dehydrocyclization to yield cycloarenes with different cavity sizes as well as a nitrogen-doped gulf-edge graphene nanoribbon. Ring formation of six precursor molecules leads to a flat cycloarene, which can host a metal atom in its central cavity. Filling the cavity causes an energetic shift of the cycloarene's frontier orbitals. The direction of the shift depends on the metal used. A curved cycloarene emerges from a ring formed by five precursor molecules, whereas a higher surface coverage favors chain formation. The electronic and geometric properties of the products were investigated by low-temperature scanning tunneling microscopy/spectroscopy (STM/STS) and non-contact atomic force microscopy (nc-AFM).

O 20.7 Tue 12:15 HE 101

Screening Nonalternant π-Electron Systems for Metal-Organic Interfaces: Interplay between Topology, Aromaticity, and Adsorption Behavior — •Jakob Schramm and Ralf Tonner-Zech — Wilhelm-Ostwald-Institut, Universität Leipzig, Deutschland

Metal-organic interfaces play an important role in organic electronics. Topology, aromaticity and interface properties are closely related as previously shown by experimental and theoretical studies of isomer pairs of nonalternant and alternant adsorbates. While nonalternant azulene and azupyrene chemisorb on Cu(111), the alternant isomers naphthalene and pyrene physisorb.[1,2]

This promises to be a general trend and can be exploited for interface design. Therefore, we utilize first-principles in-silico screening on a set of nonalternant and alternant molecules. We report data on molecular properties, especially aromaticity, based on simple topological approaches as well as DFT gas phase calculations. Furthermore, interface properties on the Cu(111) surface are reported based on periodic DFT calculations using a slab approach. We are able to show that interface properties are determined by corresponding gas phase properties which can already be derived from simple topological considerations.

[1] B. P. Klein, R. Maurer, R. Tonner, C. Kumpf, I. Swart, J. M. Gottfried et al., Phys. Rev. X. 2019, 9, 011030. [2] B. P. Klein, R. Maurer, G. Hilt, R. Tonner-Zech, A. Schirmeisen, J. M. Gottfried et al., ACS Nano 2022, 16, 11979-11987.

O 20.8 Tue 12:30 HE 101

On-Surface Synthesis of Nanostructures With Non-Alternant Topology — •Lukas Heuplick[1], Qitang Fan[1], Alexander Ihle[2], Pengcai Liu[3], Miguel Wiche[2], Xing-Yu Chen[3], Jiawen Cao[3], Jan Herritsch[1], Daniel Ebeling[2], Xiao-Ye Wang[3], André Schirmeisen[2], and J. Michael Gottfried[1] — [1]Department of Chemistry, University of Marburg, Marburg, Germany — [2]Institute of Applied Physics (IAP), University of Gießen, Gießen, Germany — [3]State Key Laboratory of Elemento-Organic Chemistry, Nankai University, Tianjin, China

In contrast to benzenoid and alternant structures, molecules with non-alternant binding motifs, such as azulene, show drastic changes in their electronic and optical properties. Acepleiadylene (APD), a constitutional isomer of pyrene, consists of 5-, 6-, and 7-membered rings and represents such a non-alternant structure. Here, we report the sucessful on-surface synthesis of nanostructures with non-alternant topology based on APD derivatives. Upon annealing 1,2-dibromoacepleiadylene on Ag(111), non-alternant nanographenes, most notably a covalent trimer, are formed by an Ullmann coupling. Annealing 1,2-dicyanoacepleiadylene on Cu(111), on the other hand, yields acepleiadylenocyanine - a phthalocyanine with non-alternant backbone - by cyclotetramerization. To characterize these reactions, we performed scanning tunneling microscopy (STM) and x-ray photoelectron spectroscopy (XPS) experiments. To provide further evidence of the actual structures, we used non-contact atomic force microscopy (nc-AFM).

O 20.9 Tue 12:45 HE 101

Deceptive orbital confinement at the edges and pores of carbon-based 1D and 2D nanoarchitectures — •Ignacio Piquero-Zulaica[1], Eduardo Corral-Rascón[1], Xabier Diaz de Cerio[2], Alexander Riss[1], Aran Garcia-Lekue[2], Hiroshi Sakaguchi[3], Willi Auwärter[1], and Johannes V. Barth[1] — [1]Physics Department E20, Technical University of Munich, D-85748 Garching, Germany — [2]Donostia International Physics Center (DIPC), E-20018 Donostia-San Sebastian, Spain — [3]Institute of Advanced Energy, Kyoto University, 611-0011, Kyoto, Japan

The electronic structure defines the properties of graphene-based nanomaterials. Scanning tunneling microscopy/spectroscopy (STM/STS) experiments on graphene nanoribbons (GNRs), nanographenes and nanoporous graphene (NPG) often determine an apparent electronic orbital confinement into the edges and nanopores, leading to dubious interpretations such as image potential states or super-atom molecular orbitals. Here we show that these measurements are subject to a wave function decay into the vacuum that masks the undisturbed electronic orbital shape. We use Au(111)-supported semiconducting gulf-type GNRs and NPGs as model systems fostering frontier orbitals that appear confined along the edges and nanopores in STS measurements. DFT calculations confirm that these states originate from valence and conduction bands. The deceptive electronic orbital confinement observed is caused by a loss of Fourier components, corresponding to states of high momentum. This effect can be generalized to other 1D and 2D carbon-based nanoarchitectures.