O 77: Nanostructures at surfaces:1D, 2D, networks II

Time: Thursday 10:30–12:15 Location: HSZ/0204

O 77.1 Thu 10:30 HSZ/0204

Interplay of flexibility, coverage, and host-guest interaction in the self-assembly of Tris(4-carboxyphenyl)amine (TCA) on Au(111) — Vishakya Jayalatharachchi[1], •Paul Philip Schmidt[1], Roberto Robles[2], Nicolas Lorente[2], Meike Stöhr[1,3], and Sabine Maier[1] — [1]Department Physik, FAU Erlangen-Nürnberg, Erlangen, Germany — [2]CFM/MPC (CSIC-UPV/EHU), Donostia-San Sebastián, Spain — [3]University of Applied Sciences of the Grisons, Switzerland

Triphenylamine derivatives are attractive building blocks for molecular architectures owing to their strong electron-donating properties, structural versatility, and ability to form highly ordered structures. Here, we explore how the non-planar and conformationally flexible arms of the unbridged threefold-symmetric TCA influence its self-assembly on Au(111), with particular emphasis on the formation and stability of porous networks. Using a combination of STM, LEED, and DFT, we show that RT deposition of TCA on Au(111) produces a coexistence of hexagonal porous domains and close-packed structures. Upon subsequent annealing, well-ordered porous networks emerge, stabilized by the dimeric carboxylic acid bonding motif. At higher coverage, this motif persists but instead directs the formation of close-packed assemblies. These findings provide insights into the interplay between molecular flexibility, intermolecular interactions, and coverage in directing supramolecular architectures of unbridged triphenylamines on metal surfaces. In addition, we show on the example of molecular rotors the hosting properties of the porous TCA network.

O 77.2 Thu 10:45 HSZ/0204

Revealing and manipulating correlated protons in one-dimensional hydrogen-bonded chains at the atomic scale — •Yiqi Zhang — Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China

Hydrogen-bonded systems such as water and ice exemplify highly cooperative proton dynamics, where covalent bonds are broken and formed in a concerted fashion. Yet directly probing and controlling many-body proton configurations at the atomic scale remains challenging. Here, using bond-resolved atomic force microscopy and spectroscopy, we reveal multistate proton ordering in self-assembled one-dimensional chains of an imidazole derivative on a noble metal surface. In as-grown chains of varying length, we consistently identify an interior species bonded to an extra proton, forming a localized imidazolium cation (state 1). Selective removal of a single proton from either chain end triggers a collective rearrangement of protons, yielding unidirectional hydrogen-bonding along the entire chain (states 2 or 3). Further deprotonation creates a proton vacancy, enabling reversible switching of hydrogen-bonding directionality (states 4 and 5) via collective proton hopping above a threshold bias voltage. In conjunction with density functional theory calculations, we elucidate the microscopic origin of complex proton ordering in hydrogen-bonded chains and the correlated motion of multiple protons.

O 77.3 Thu 11:00 HSZ/0204

On-Surface Synthesis of a Janus Polyazaacene — •Faming Kang, Tim Naumann, Zilin Ruan, Ye Liu, and J. Michael Gottfried — Fachbereich Chemie, Philipps-Universität Marburg, Hans-Meerwein-Str. 4, 35032 Marburg, Germany

Acenes are a fascinating class of polycyclic aromatic hydrocarbons that have gained considerable research interest due to their potential application in organic electronics as well as their role in advancing fundamental knowledge about conjugated aromatic systems. Isosteric exchange of CH units of the acenes by nitrogen atoms formally gives azaacenes. The nitrogen substitution pattern, i.e., the number, position, and type of nitrogen atoms enables topological design of azaacenes, which facilitates precise tuning of frontier orbital energy level alignment and radical characters. Guided by topological considerations, introducing distinct edge structures on either side further creates Janus azaacenes. Here, we successfully synthesized a Janus polyazaacene on the Au(111) surface, in which one edge was decorated by nitrogen atoms while the other edge keeping unchanged. The length of such a polymer chain can reach up to 50 rings. Using scanning tunneling microscopy, we characterized its geometric structure and electronic property on Au(111), as well as its stability in air.

O 77.4 Thu 11:15 HSZ/0204

Modeling the Registry of Molecular Adsorbates on Solid Surfaces — •David Ari Hofmeister[1], Christian Erik Selzer[2], Laura zur Horst[1], Simon Christian Rickert[1], Julia Kohn[2], Andreas Hansen[2], Stefan-Sven Jester[1], and Sigurd Höger[1] — [1]Kekulé-Institut für Organische Chemie und Biochemie, Rheinische Friedrich-Wilhelms-Universität Bonn, Bonn (Germany) — [2]Mulliken Center for Theoretical Chemistry, Rheinische Friedrich-Wilhelms-Universität Bonn, Bonn (Germany)

Rationalizing the adsorption behavior of large organic molecules on crystalline substrates is crucial for the design of functional surfaces in supramolecular chemistry, catalysis, and electronics. Conventional quantum-chemical approaches often fail for large π-conjugated systems due to their size and conformational flexibility. Here, we present a physically intuitive and generalizable method that overcomes these limitations by optimizing the molecular registry through a geometry-based strategy: maximizing the overlap between surface-oriented hydrogen atoms ("spikes") and the periodic "pockets" defined by the hexagon centers of HOPG. Inspired by the Groszek alkane-on-graphite model, our approach extends to structurally complex architectures and assigns adsorption geometries with high resolution without costly computations. Combining registry scoring with STM data allows the determination of absolute atropisomer conformations, demonstrating that geometric registry is a broadly applicable metric for predicting the surface arrangements of large molecules.

O 77.5 Thu 11:30 HSZ/0204

Low Dimensional Assemblies of Endohedral Fullerenes on Surfaces — •Lukas Emanuel Spree[1,2], Caroline Hommel[1,2], Pierre Josse[1,2], Justyna Piwowar[1,2], Robert Ranecki[1,2], and Andreas Heinrich[1,3] — [1]IBS Center for Quantum Nanoscience, Seoul, South Korea — [2]Ewha Womans University, Seoul, Republic of Korea — [3]Department of Physics, Ewha Womans University, Seoul, Republic of Korea

Scanning probe microscopy techniques like STM and AFM facilitate the characterization of atoms and molecules on flat substrates with nearly unrivaled spatial resolution. Utilizing the strengths of these techniques, our team is looking to build custom molecular structures in a bottom-up manner and characterize their physical properties.

The main focus of this work is on endohedral fullerenes, a class of compounds that facilitate the stabilization of exotic configurations of few-atom structures within a carbon cage. Among them are some of the best single molecule magnets discovered to date, as well as promising candidates for spin-qubits. These desirable traits are combined with very high chemical stability. Utilizing the physical properties of these fascinating compounds is limited by two main issues: synthetic yield and, to a lesser degree, crystalline order. Both can be addressed elegantly by focusing on their properties in low dimensional arrangements, like monolayers or single molecules on ultraflat surfaces.

In this presentation we will detail our ongoing efforts of utilizing a broad range of deposition techniques, molecule manipulation on the surface, and chemical self-assembly approaches.

O 77.6 Thu 11:45 HSZ/0204

Electronic Modulation by the Sc3N Cluster in Endohedral Fullerene Sc3N@C80 — •Seong-Hyun Hong[1,4], Dmitriy Borodin[1,2], Lukas Spree[1,2], Andrés Pinar Solé[1,2], Caroline Hommel[1,2], Merve Ercelik[1,2], Shinjae Nam[1,2], Robert Ranecki[1,2], Fabio Donati[1,3], Se-Jong Kahng[4], and Andreas Heinrich[1,3] — [1]Center for Quantum Nanoscience (QNS), Institute for Basic Science (IBS) — [2]Ewha Womans University — [3]Department of Physics, Ewha Womans University — [4]Department of Physics, Korea University

Endohedral fullerenes such as Sc3N@C80 present a unique platform to study confined molecular systems, where the behavior of an enclosed cluster can strongly influence the properties of the surrounding cage. Understanding how the Sc3N cluster interacts with the carbon framework at the submolecular level is essential, but direct observation of these interactions remains challenging due to existence of carbon cage.

Here, we combine low-temperature scanning tunneling microscopy (STM) and atomic force microscopy (AFM) with a CO-functionalized tip to investigate Sc3N@C80. Using scanning tunneling spectroscopy

(STS) and Kelvin probe force microscopy (KPFM), we map the charge distribution across the fullerene with submolecular resolution, revealing how the Sc3N cluster modulates the electronic structure of the cage. This approach provides significant insight into the interplay between core position and molecular charge distribution, uncovering details of the inner cluster that were previously unclear.

O 77.7 Thu 12:00 HSZ/0204

Ferroelectric vortices in elemental Bismuth square islands — •Shasha Xue and Hao Zheng — Tsung-Dao Lee Institute, Shanghai Jiao Tong University, Shanghai, China

Ferroelectric vortices, with their unique topological polarization patterns, show great potential for next-generation electronics. Although they have been observed in compounds, their realization in single-element materials has remained elusive. Here, we experimentally prepare three-bilayer Bi(110) square-shaped islands on high-T_C superconductor ($Bi_2Sr_2CaCu_2O_{8+\delta}$) substrates by molecular beam epitaxy. Scanning tunneling microscopy/spectroscopy combined with first-principal calculations verify in-plane polarization and a ferroelectric vortex state in our islands, as well as reveals exceptional vortex stability against electric-field-driven switching. This work pioneers single-element ferroelectric vortices, advances topological ferroelectrics design and expands the understanding in related fundamental physics.