O 87: Focus Session: Molecular Nanostructures on Surfaces: On-Surface Synthesis and Single-Molecule Manipulation III

Time: Thursday 15:00–18:00 Location: HE 101

Topical Talk O 87.1 Thu 15:00 HE 101

Towards the third dimension: Organic molecular architectures synthesized on solid surfaces by means of solution-based click chemistry — •Michael Dürr — Institut für Angewandte Physik and Zentrum für Materialforschung, Justus-Liebig-Universität Giessen, Germany

In most on-surface reactions, the solid (metal) substrate acts both as a template as well as a catalyst. When we think on expanding the concept of on-surface synthesis into the third dimension, the coupling reactions will not be catalyzed by the substrate any more. Thus, either catalyst-free reaction schemes or new reaction strategies have to be applied. For the growth of 3D structures on silicon surfaces, we have followed two alternative routes: Using a carefully tuned enolether/tetrazine cycloaddition, a second layer of organic molecules was directly coupled under UHV conditions on a prefunctionalized Si(001) surface. As an alternative approach, we combined UHV-based surface functionalization with solution-based click chemistry. In this scheme, ordered multilayers of organic molecules were realized on the prefunctionalized Si(001) surface via a two-step reaction cycle in solution. In order to ensure a controlled layer-by-layer growth, two orthogonal alkyne-azide click reaction schemes based on asymmetric bifunctional molecular building blocks were employed. Each reaction step was monitored by means of XPS demonstrating a high selectivity of the reaction schemes in use. Our approach thus opens the road for the controlled synthesis of organic 3D structures on surfaces.

O 87.2 Thu 15:30 HE 101

Probing dynamic covalent chemistry in a 2D boroxine framework — Paul Leidinger[1], Mirco Panighel[2], Virginia Pérez-Dieste[3], Ignacio Villar-Garcia[3], Pablo Vezzoni[1], Felix Haag[1], Johannes V. Barth[1], Francesco Allegretti[1], Sebastian Günther[1], and •Laerte L. Patera[1,4] — [1]Technical University of Munich, Garching, Germany — [2]CNR-IOM, Trieste, Italy — [3]CELLS-ALBA, Cerdanyola del Valles, Spain — [4]University of Innsbruck, Innsbruck, Austria

The use of dynamic covalent chemistry provides a powerful method for designing covalent organic frameworks, exploiting reversible bond formation to achieve remarkable crystallinity. Here we employed near-ambient pressure X-ray photoelectron spectroscopy to dissect the reversible construction of a two-dimensional boroxine framework on a Au(111) surface. By mapping the pressure-temperature parameter space, we identified the regions where the rates of the condensation and hydrolysis reactions become dominant. This precise identification is critical for enabling thermodynamically controlled growth of highly crystalline frameworks [1]. [1] P. Leidinger, et al., Nanoscale 15, 3, 1068-1075 (2023).

O 87.3 Thu 15:45 HE 101

The Chemical Functionalization of the Biphenylene Network predicted by DFT — •Hendrik Weiske and Ralf Tonner-Zech — Universität Leipzig, Leipzig, Deutschland

2D materials, such as graphene, could introduce a new disruptive technology, replacing some of the currently used materials. The covalent functionalization of graphene is still relatively uncommon and limited to powerful reagents, e.g., free radicals, *n*-BuLi, or strong nucleophiles.[1] The biphenylene network (BPN) is a recently synthesized 2D material[2] with a promising application range, from photocatalysis to superconductivity. While hydrogenated or fluorinated derivatives of BPN are discussed in the literature already, the molecular functionalization is an unexplored topic in the field. We show that the unique electronic structure of BPN enables functionalization using the stable unsaturated cyclic hydrocarbon cyclooctyne. Cyclooctyne is known to form well-ordered layers on Si(001), which we studied extensively in the past.[3,4] We propose cyclooctyne as a promising molecule to functionalize BPN towards new properties. We extensively studied the adsorption kinetics of cyclooctyne, thermodynamics, chemoselectivity for the reaction, and its effect on the electronic structure.

[1] I. A. Vacchi, A. Bianco, et al., Phys. Sci. Rev., **2017**, *2*. [2] Q. Fan, A. S. Foster, U. Koert, P. Liljeroth, J. M. Gottfried, et al., Science **2021**, *372*, 852-856. [3] F. Pieck, R. Tonner-Zech, Molecules, **2021**, *26*, 6653 [4] L. Pecher, R. Tonner, et al., J. Phys. Chem. C, **2017**, *121*, 26840-26850

O 87.4 Thu 16:00 HE 101

Reactivity of Aromatic Amines on Metal Surfaces — Nan Cao[1,2], Kaifeng Niu[3], Wenchao Zhao[2], Jonas Björk[3], Lifeng Chi[1], Johannes Barth[2], and •Biao Biao[1,2] — [1]Soochow University, Suzhou 215123 (P. R. China) — [2]Technical University of Munich, D-85748 Garching, (Germany) — [3]Linköping University, 58183 Linköping (Sweden)

Aromatic amines are widely used as intermediates to dyes, pharmaceuticals, and agricultural chemicals, whereas the oxidation process is of great significance for their direct application and synthesis of other complex nitrogen-containing compounds. Dehydrogenation of the amino group in aromatic amines on copper surfaces is usually achieved with thermal treatment. However, amino has no reactivity reported on relatively inert surfaces of silver and gold. Herein, we combine STM and XPS studies to explore the reactivity of aromatic amines on silver and gold surfaces with the O2-gas mediation[1]. While oxidative dehydrogenation reaction is achieved on silver surfaces, forming the N-Ag complex with intrinsic Ag adatoms, aromatic amine layers remain intact on the gold surface with the O2-mediated treatment. Complementary insights from density functional theory calculations of reaction pathway, core level shift, and chemisorption energy reveal the thermodynamically substrate-dependent mechanics. The systematic study unveils the mechanism of catalytic oxidative dehydrogenation reaction of amines, enriching the on-surface synthesis toolbox for the production of low-dimensional organic materials. Reference [1] Nan Cao, Biao Yang et al. Nat. Commun. 14, 1255 (2023)

O 87.5 Thu 16:15 HE 101

An alternative on-surface synthesis approach on Ag(111) studied by STM and XPS — •Paul Schweer[1], Christoph Vonnemann[2], Stefan Huber[2], and Karina Morgenstern[1] — [1]Chair of Physical Chemistry I, Ruhr University of Bochum, Germany — [2]Chair of Organic Chemistry II, Ruhr University of Bochum, Germany

On-surface synthesis uses planar precursors containing carbon atoms that are sp2 hybridized and halogen functionalized to construct 2D structures by thermal activation. The mechanism includes the cleavage of the carbon-halogen bond, followed by an intermolecular C-C coupling. In this talk, we will present an alternative approach based on a polyaromatic molecule with a single sp3 hybridized fluorinated carbon atom as the reactive center. The reaction is induced by thermal and photoactivation on Ag(111). We describe the self-assembly of the molecules and the mechanisms of their on-surface reaction by means of scanning tunneling microscopy and X-ray photoelectron spectroscopy investigations. These results give insights into an intramolecular reaction pathway that produces single cyclized structures.

O 87.6 Thu 16:30 HE 101

Functionalization of Surfaces with Ordered Arrays of Endohedral Fullerenes — •Lukas Spree, Caroline Hommel, Luciano Colazzo, and Andreas Heinrich — IBS Center for Quantum Nanoscience, 52 Ewhayeodae-gil, Daehyeon-dong, 03760 Seoul, South Korea

Endohedral fullerenes are hollow, sperical carbon structures, that can encase and protect very exotic configurations of certain elements. Confining several atoms inside the carbon cage leads to a unique combination of desirable physical properties, chemical stability, and tunability. Studies of endohedral fullerenes in bulk have yielded some very promising single molecule magnets and spin-qubit candidates.

Making these fascinating compounds accessible to characterization and manipulation by scanning probe microscopy techniques is challenging. Short range order can often not be achieved, because freely rotating encapsulated species and energetically similar configurations of the cages on the substrate offer high degrees of freedom. This leads to variance in the magnetic and coherent properties of the individual molecules.

Chemical functionalization of the fullerene cages and the use of template layers made of tetrapyrroles like porphyrines offer a way to reduce the number of possible configurations.

The combination of different molecular species on metallic substrates in ultrahigh vacuum requires the use of various deposition techniqes. Electrospray deposition, sublimation, and formation of monolayers at substrate-solution interfaces are discussed.

O 87.7 Thu 16:45 HE 101

Low temperature atomic force microscopy with an adaptive tunneling current feedback for simultaneously visualizing chemical structures and adsorption positions of organic molecules — Daniel Martin-Jimenez[1,2,3], Qigang Zhong[1,2], André Schirmeisen[1,2], and •Daniel Ebeling[1,2] — [1]Institute of Applied Physics (IAP), Justus Liebig University Giessen, Germany — [2]Center for Materials Research (LaMa), Justus Liebig University Giessen, Germany — [3]Institut de Ciencia de Materials de Barcelona (ICMAB-CSIC), Campus Bellaterra, Barcelona, Spain

Low temperature atomic force microscopy with CO-functionalized tips allows to visualize the chemical structure of adsorbed organic molecules. This tool became essential for the field of on-surface synthesis as it enables revealing the structures of the products and corresponding reaction mechanisms. Established methods for determining adsorption positions of precursors, intermediates, and products, which are important for a direct comparison with calculated adsorption structures, however, remain rather complex and time-consuming. Here, we illustrate a relatively simple method that can be used to simultaneously visualize the chemical structure of organic molecules and surface atoms in a single scan. The proposed method is based on automatically switching between different tunneling feedback parameters, which are optimized for the two different tasks. Switching between feedback parameters allowed to reliably image highly mobile 2-iodotriphenylenes on a Ag(111) surface with sub-molecular resolution and precisely determine the positions of Ag(111) top sites in their close vicinity.

O 87.8 Thu 17:00 HE 101

NC-AFM characterization of single-atom catalytic sites within metal-coordinated supramolecular networks — Bertram Schulze Lammers[1], Nieves López-Salas[2], Julya Stein Siena[2], Hossein Mirhosseini[3], Damla Yesilpinar[1], Julian Heske[3], Thomas D. Kühne[3], Harald Fuchs[1], Markus Antonietti[2], and •Harry Mönig[1] — [1]Physikalisches Institut, Universität Münster — [2]Max Planck Institute of Colloids and Interfaces, Potsdam — [3]Theoretical Chemistry, Universität Paderborn

For the development of single atom catalysts, non-noble metal-organic layers combine functional variability with cost efficiency. Here we investigated reacted layers of melamine and melem on a Cu(111) surface by NC-AFM with CuOx-functionalized tips [1]. Upon deposition and subsequent heat treatments, the molecular units are completely deprotonated and adsorb flat and strongly chemisorbed. We observe a particularly extreme interaction of the deprotonated N- with single Cu atoms located at intermolecular sites. The NC-AFM measurements and ab-initio simulations indicate a pronounced interaction of O-species at these N-Cu-N sites. To study potential catalytic properties, we performed cyclic voltametry experiments on our samples at ambient pressure within a drop of electrolyte in a controlled O_2 or N_2 environment. Both Cu-nitride structures show a robust activity in irreversibly catalyzing the reduction of oxygen. The activity is assigned to the intermolecular N-Cu-N sites or corresponding oxygenated versions (N-CuO-N, N-CuO_2-N) [2]. [1] H. Mönig, ChemComm 54, 9874 (2018); [2] B. Schulze Lammers et al., ACS Nano 16, 14284 (2022).

O 87.9 Thu 17:15 HE 101

On-Surface Synthesis of Oxygen Annulated Porphyrins — •Joel Deyerling[1], Beatrice B. Berna[2], Dmytro Biloborodov[2], Felix Haag[1], Sena Tömekce[1], Marc G. Cuxart[1], Davide Bonifazi[2], and Willi Auwärter[1] — [1]Physics Department E20, TUM School of Natural Sciences, Technical University of Munich, Garching, Germany — [2]Institute of Organic Chemistry, Faculty of Chemistry, University of Vienna, Vienna, Austria

Recently the on-surface synthesis of fused porphyrins through C-H activation followed by C-C bond formation has generated considerable interest [1-3]. These porphyrins afford various edges and topologies, thus, offering precise control of their functional properties. From a chemistry point of view, the toolbox is currently limited to C-C coupling, while on-surface C-heteroatom fusing to porphyrins is elusive.

In this context we explore the on-surface oxygen annulation of Ni(II)-tetra- and octahydroxyporphyrins on Au(111). Upon thermal activation, the ortho-positions of the meso-aryl substituents (dihydroxyphenyls) are connected by an O-bridge to the β-pyrrolic positions of the porphyrin macrocycle, creating pyran rings. Employing STM, nc-AFM and high-resolution XPS, we provide a comprehensive characterization of the on-surface reaction. Beyond that, we elucidate how the oxygen tailors the electronic structure and drives the assembly of the achiral molecules into chiral lattices.

[1] Sun, Q. et al., JACS, 142, 18109-18117 (2020).
[2] Yang, X.-Q. et al., ACS Nano, 16, 13092-13100 (2022).
[3] Deyerling, J. et al., J. Phys. Chem. C, 126, 8467-8476 (2022).

O 87.10 Thu 17:30 HE 101

A temperature-programmed X-ray photoelectron spectroscopy study of a halogenated porphyrin on Au(111) and Cu(111) — •Michael Clarke[1], Eleanor Frampton[2], Matthew Edmondson[1], Ailish Gray[1], Jonathan Bradford[1], and Alex Saywell[1] — [1]School of Physics & Astronomy, University of Nottingham, UK — [2]MAX IV Laboratory, Lund, Sweden

Halogenated porphyrins on metallic surfaces undergo a variety of reactions when heated, such as Ullmann-type coupling, ring-closing, metalorganic coordination, and self-metalation. These reactions are influenced by various factors, including porphyrin and substrate chemistry.[1] Porphyrins are of interest as precursor monomers in on-surface assembly, due to their tuneable optoelectronic and gas absorption properties.[2] Here, we detail the reaction of a brominated porphyrin (BrxTPP) on Au(111) and Cu(111), via near edge X-ray absorption fine structure (NEXAFS), X-ray photoelectron spectroscopy (XPS) and scanning tunnelling microscopy (STM). Building upon our previous work, [3,4] temperature programmed XPS (TP-XPS) provides a detailed characterisation of the molecular structure to be obtained as the reaction progresses. The chemistry, orientation, and conformation of the porphyrins is explored.

[1] L. Grill, S. Hecht, Nat. Chem. 12, 115 (2020) [2] E. Vesselli, J. Phys. Mater. 3, 022002 (2020) [3] M. Edmondson, E.S. Frampton, C.J. Judd, N.R. Champness, R.G. Jones and A. Saywell, Chem. Commun., 2022, 58, 6247. [4] E.S. Frampton, M. Edmondson et al., Inorganica Chim. Acta, 558, 121718, (2023)

O 87.11 Thu 17:45 HE 101

On-Surface Reaction of Tetraphenylporphyrin with Caesium — •Leonard Neuhaus, Florian Münster, Kassandra Zoltner, Lukas Heuplick, Jan Herritsch, and J. Michael Gottfried — Department of Chemistry, University of Marburg, 35043 Marburg, Germany

Tetrapyrroles such as porphyrins and their metal complexes play important roles in living organisms and in modern technologies, e.g., in energy storage, (electro-)catalysis and sensor systems. While transition metal complexes of tetrapyrroles on surfaces have been well studied in the last decades, much less is known about their complexes with alkali metals. Here, we report studies of the reaction of tetraphenylporphyrin (H2TPP) with vapor-deposited caesium in the multilayer and (sub)monolayer regimes on Ag(111). XPS indicates for the submonolayer and multilayer partial metalation to Cs2TPP already at 300 K, whereas in monolayer regime no reaction is observed at this temperature. STM however, shows that the Cs atoms still coordinate to the porphyrin molecules at 300 K. After annealing to 400 K full conversion is observed. DFT calculations suggest that the Cs2TPP complex has a bipyramidal structure with Cs ions on both sides of the molecular plane, which is in line with STM measurements. In complementary temperature-programmed reaction (TPR) experiments, the desorbing species were clearly identified by mass spectrometry as Cs2TPP. TPR also indicates that Cs2TPP is thermally stable up to at least 700 K.