# O 17: Poster Focus Session Molecular Nanostructures on Surfaces: On-Surface Synthesis and Single-Molecule Manipulation

Time: Monday 18:00–20:00 Location: P2

O 17.1 Mon 18:00 P2

**Synthesis and characterization of a non-planar cyclophenylene on Au(111)** — Sergio Salaverria[1], Martin Irizar[2,3,4], Jesus Janeiro[5], Paula Angulo-Portugal[6], Tao Wang[2], Jan Patrick Calupitan[6], •Jonathan Rodriguez-Fernandez[1,7], Aran Garcia-Lekue[2,8], Martina Corso[6], Emilio Artacho[2,3,8,9], Diego Peña[5], Dolores Perez[5], and Dimas G. de Oteyza[1,2] — [1]CINN, CSIC-UNIOVI-PA, El Entrego, Spain — [2]DIPC,San Sebastián, Spain — [3]CIC nanoGUNE, San Sebastián, Spain — [4]PMAS, UPV/EHU, San Sebastián, Spain — [5]CiQUS, Universidade de Santiago de Compostela, Spain — [6]CFM-MPC, CSIC-UPV/EHU, San Sebastián, Spain — [7]Physics Department, University of Oviedo, Spain — [8]Ikerbasque, Basque Foundation for Science, Bilbao, Spain — [9]TCM, University of Cambridge, Cambridge (UK)

Cyclophenylenes, i.e., macrocycles composed of linked benzene rings, have attracted intensive interest because of their appealing structures and potential applications.

In this work, we report the on-surface synthesis of a non-planar Au-coordinated cyclophenylene, containing four meta- and two para-connections, on a Au(111) surface, by undergoing hierarchical, metal-assisted double Ullmann coupling of a 1,10-dibrominated angular phenylene, and subsequent selective C-C bond cleavage of the four-membered rings in the resulting phenylene dimer. The chemical structure was characterized by bond-resolving (BR) STM and further supported by STS and DFT. This study offers the first approach for the synthesis of non-planar cyclophenylenes on surfaces.

O 17.2 Mon 18:00 P2

**Experimental benchmark for configuration monitoring during scanning-probe-microscope manipulation** — •Mong-Wen Gu[1], Jonas Lederer[2], Joshua Scheidt[1,2], Hadi H. Arefi[1], Kristof T. Schütt[2], Michael Gastegger[2], F. Stefan Tautz[1], Klaus-Robert Müller[2], and Christian Wagner[1] — [1]Peter Grünberg Institut (PGI-3), Forschungszentrum Jülich, Jülich, Germany — [2]Machine Learning Group, Technische Universität Berlin, Berlin, Germany

The scanning probe microscope (SPM) allows nano-objects to be manipulated with single-molecule precision. A critical challenge of this SPM-based technique is to simultaneously manipulate molecules and monitor their configuration. Here, an experimental protocol is developed and evaluated that predicts the molecular configuration based on the physical observables continuously acquired by the SPM. A PTCDA (3,4,9,10-perylene tetracarboxylic dianhydride) molecule on the Ag(111) surface is manipulated to move along a predefined tip trajectory. The measured observables (force gradient) are compared with the results of a DFT trained machine learning model. This work paves the way for the fabrication of a wide variety of nanostructures.

O 17.3 Mon 18:00 P2

**Exploring supramolecular rings by scanning tunneling microscopy** — •Cagri Turan[1], Elie Benchimol[2], Guido Clever[2], and Karina Morgenstern[1] — [1]Physical Chemistry I, Ruhr-Universität Bochum, Germany — [2]Inorganic Chemistry, Technische Universität Dortmund, Germany

Enzymes inspire the design of supramolecular systems, mimicking their catalytic functions for advanced material applications. Among these systems, supramolecular rings and cages are one of the most suitable candidates for mimicking enzyme-like behavior. The use of two different ligands in the heteroleptic supramolecular rings enhances their complexity, enabling the creation of structures that resemble the sophisticated architectures of enzymes. This study reports deposition, self-assembly and inelastic electron tunneling manipulation of PdL2 rings on the Ag(111) surface. The ring molecules were characterized using low-temperature scanning tunneling microscopy in ultra-high vacuum at 7 K. By utilizing an atomic layer injection system, the acetonitrile solvent, used as a solvent during the self-assembly of ligands, will evaporate before the molecules reach the surface, ensuring that only the ring molecules are deposited onto the substrate. Through inelastic electron tunneling manipulation, site-specific manipulations and ligand dissociation processes were explored, offering insights into reaction mechanisms and molecular dynamics on rings on the metallic substrate. The findings contribute to understanding the interaction of supramolecular systems with metal surfaces, enabling advancements in nanoscale functional materials.

O 17.4 Mon 18:00 P2

**Autonomous chemical reactions in scanning tunneling microscopy** — •Nian Wu[1], Peter Liljeroth[1], and Adam S. Foster[1,2] — [1]Department of Applied Physics, Aalto University, Espoo, Finland — [2]WPI Nano Life Science Institute, Kanazawa University, Kanazawa, Japan

Scanning tunneling microscopy (STM) has shown great promise in manipulating atoms or molecules in on-surface molecular synthesis. However, the selection of proper parameters for various manipulations requires extensive explorations and strongly depends on domain knowledge. In particular, the coupling of fragments, as a critical step for polymerizations, necessitates more precise control in rotations and distances. To address this problem, we designed a deep reinforcement learning approach to automate the C-C coupling from Zn(II)-5,15-bis(4-bromo-2,6-dimethylpheny)porphyrin (ZnMe4DPP2.) through learning manipulation parameters in STM, thus enabling the assembly of large polymers based on the building blocks.

O 17.5 Mon 18:00 P2

**Steering intermolecular interaction and ordering of N-heterocyclic carbenes on metal surfaces** — •Duong Tran[1,2], Philipp Wiesener[1,2], Lacheng Liu[1,2], Ankita Das[3], Alex-Cristian Tomut[4], Nikos Doltsinis[4], Frank Glorius[3], Harald Fuchs[1,2], and Harry Mönig[1,2] — [1]Physikalisches Institut, Universität Münster, Wilhelm-Klemm-Straße 10, 48149 Münster, Germany — [2]Center for Nanotechnology, Heisenbergstraße 11, 48149 Münster, Germany — [3]Organisch-Chemisches Institut, Universität Münster, Corrensstrasse 40, 48149 Münster, Germany — [4]Institut für Festkörpertheorie, Universität Münster, Wilhelm-Klemm-Straße 10, 48149 Münster, Germany

N-Heterocyclic carbenes (NHCs) are established ligands for the chemical and electronic functionalization of surfaces and nanoparticles. Controlling their nucleation and aggregation mechanisms provides valuable opportunities to tune their catalytic- and electro-optical properties. In the present work, we investigate the effect of hydroxyl-side groups on the self-assemblies of IMes on Au(111) and Ag(111) substrates by scanning tunneling microscopy with sub-molecular resolution. Our results are complemented by X-ray photoelectron spectroscopy (XPS) and first-principles calculations. We find that the OH groups can drastically enhance the molecular order, especially on the Ag(111) substrate where extended 2D networks are found. Our findings are essential for robust NHC-based supramolecular networks with tailored properties.

O 17.6 Mon 18:00 P2

**Controlling on-surface chemical reactions through photochemistry** — •Hao Jiang, Yu He, Jiayi Lu, Zhiwen Zhu, and Qiang Sun — Materials Genome Institute, Shanghai University, 200444 Shanghai , China

On-surface synthesis targets extended nanostructures by covalent coupling of organic molecules on surfaces. The most common way to induce reactions of precursor molecules on the surface is by heating, which will however increase the possibility of forming side reactions and lacks selectivity in many cases, thus limiting wider applications of on-surface synthesis. In contrast to the thermally triggered chemistry, photochemistry provides an alternative way to activate molecules. Light has been demonstrated to break certain covalent bonds in a less constructive fashion. Moreover, light has more adjustable parameters such as intensity, wavelength, polarization, etc., to control reactions more finely. Recently, we demonstrated the use of light polarizations to reveal the mechanism of dehalogenation reaction and realized photo induced dechlorination reactionon metal surfaces.

In this poster, we will showcase the wavelength dependence in on-surface synthesis and demonstrate how to harness photochemistry to achieve reaction selectivity in on-surface reactions. Three organic molecules, each with the same functional group, exhibit different chemical reactivities under photon excitation. Our work provides fundamental insights into photoinduced on-surface reactions and illustrates the potential of photochemistry for achieving highly selective and controllable reactions.

O 17.7 Mon 18:00 P2

**Reaction intermediates, organometallic polymers and graphene nanoribbons in on-surface Ullmann-type coupling on coinage metals** — R.S. Koen Houtsma[1], Jeanne van Zuilen[1], Floris van Nyendaal[1], Mihaela Enache[1], and ●Meike Stöhr[1,2,3] — [1]University of Groningen, Netherlands — [2]Friedrich-Alexander-Universität Erlangen-Nürnberg, Germany — [3]University of Applied Sciences of the Grisons, Switzerland

Ullmann-type coupling has been so far the most often employed on-surface reaction for the controlled fabrication of molecular nanoarchitectures in a bottom-up manner. For the case of the prochiral precursor molecule 6,12 dibromochrysene, we compared the influence of substrate material/orientation, annealing temperature and reaction conditions on the reaction outcome. While on Au(111) achiral chevron-type graphene-nanoribbons are formed [1], on Cu(111), Ag(111) [2] and Ag(110) [3] only 1D organometallic polymers were obtained. These 1D polymers are homochiral when Cu(111) was used as substrate whereas they were heterochiral on Ag(111). In the case of Ag(110), their chirality could be even steered via the reaction conditions. With the help of reaction intermediates observed on Ag(111), we obtained key insights into the formation process of the organometallic polymers which is based on the breaking and re-establishing of C-Ag bonds. References: [1] R.S.K. Houtsma et al., Nanoscale Adv. 2022, 4, 3531. [2] R.S.K. Houtsma et al., Adv. Mater. Interfaces 2024, 11, 2300728. [3] R.S.K. Houtsma et al., Commun. Chem. 2024, 7, 51.

O 17.8 Mon 18:00 P2

**LT-STM investigations of subphthalocyanine based vertical molecular rotors on Au (111)** — ●Franz Plate[1], Natasha Khera[1], Suchetana Sarkar[1], Soyoung Park[2,3], Ningwei Sun[2,3], Ebru Cihan[1], Dmitry Ryndyk[1,4], Franziska Lissel[2,3], and Francesca Moresco[1] — [1]Center for Advancing Electronics Dresden, TU Dresden, 01062 Dresden, Germany — [2]Leibniz Institute of Polymer Research Dresden, TU Dresden, 01069 Dresden Germany — [3]Institute of Applied Polymer Physics (IAPP) TU Hamburg, Kasernenstraße 12, 21073 Hamburg Germany — [4]Professur für Theoretische Chemie, TU Dresden, 01062 Dresden, Germany

We present a vertical rotor based on borsubphthalocyaninchloride (SubPC) platforms adsorbed on Au(111), investigated by low temperature scanning tunneling microscopy. SubPC is a well-investigated molecule which is known to form well-ordered structures, to adsorb flat on the surface and to be highly mobile as a single molecule. The boron atom carries an axial ligand. In this study, SubPC was functionalized with different axial ligands, aiming to create a vertical molecular rotor. The adsorption behavior of SubPC functionalized with azobenzene and 2-methylnaphthalene after thermal evaporation and flash deposition on a cold (5K) surface is presented in high resolution STM images supported by density functional theory (DFT) simulations. In addition, the stabilization through co-deposited pure SubPC and SubPC functionalized with 2-methylnaphthalene is presented.

O 17.9 Mon 18:00 P2

**Adsorption behavior of organoboroxine and organoborthiine based molecules on Au(111)** — ●Natasha Khera[1], Franz Plate[1], Karen Marlenne Garcia Alvarez[2], Suchetana Sarkar[1], Andreas Schneemann[2], and Francesca Moresco[1] — [1]Center for Advancing Electronics Dresden, TU Dresden, 01062 Dresden, Germany — [2]Inorganic Chemistry I, TU Dresden, 01069 Dresden, Germany

In this study, we investigate the adsorption behavior of organoboroxine and organoborthiine based molecules on Au (111) surface, employing low temperature scanning tunneling microscopy (LT-STM) and spectroscopy in ultra-high vacuum (UHV) conditions. Organoboroxines provide a model system for constructing Covalent Organic Frameworks (COFs) and are well studied for their applications in catalysis, material science, optoelectronics and energy storage. In contrast, organoborthiines, due to their sulfur mediated interactions, hold promise, making them a compelling area for future research. In this work, a comparative analysis of the adsorption geometries, self-assembled structures and spectroscopic properties of both these molecules is presented.

O 17.10 Mon 18:00 P2

**Chemical activation of a single melamine molecule via isomerization and metalation with a copper atom** — ●Karl Rothe[1], Manex Alkorta[2], Nicolas Néel[1], Thomas Frederiksen[3], and Jörg Kröger[1] — [1]Institut für Physik, Technische Universität Ilmenau, D-98693 Ilmenau — [2]Centro de Física de Materiales and Fisika Aplikatua Saila, University of the Basque Country, E-20018 Donostia - San Sebastián — [3]Donostia International Physics Center, E-20018 Donostia San Sebastián and IKERBASQUE, Basque Foundation for Science, E-48011 Bilbao

The entire sequence of chemically activating an educt, identifying its reactive site, running a chemical reaction and quantifying the involved forces and energies was performed by means of scanning probe methods. The organic molecule melamine adsorbed on Cu(100) serves as a single-molecule model system for activation via tautomerization and consecutive metalation with a single Cu atom. An atomic force microscope with a CO-decorated tip probes the reactive sites of the isomers at which the subsequent single metal atom transfer is initiated using a Cu-terminated probe. Following the interaction between the mutually approached reaction partners up to the verge of chemical-bond formation enables the access to the force and energy involved in the single-molecule metalation process. Total-energy calculations from density functional theory support the experimental findings and illustrate the structure of the reactants.

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O 17.11 Mon 18:00 P2

**Metallocorroles: On-Surface Synthesis, Adsorption Geometry, and Electronic Structure** — ●Cong Guo, Jan Herritsch, Anastasiya Beliakouskaya, and J. Michael Gottfried — Philipps-Universität Marburg, Fachbereich Chemie, 35043 Marburg, Germany

Tetrapyrrolic macrocycles are widely recognized as fundamental building blocks for interfacial covalent architectures with remarkable stability and atomic precision. Corrole complexes are particularly notable due to their nature as trianionic ligands providing a contracted coordination environment. Herein, we report the on-surface formation and reaction of an octaalkyl-substituted magnesium corrole and an iron triphenylcorrole (FeTPC) on Ag(111). The free-base octaalkyl-corrole forms a well-ordered overlayer . Upon vapor deposition of Mg, the metal atoms incorporate into the corrole cavity, forming Mg-corrole complexes. However, XPS and STM studies show that excessive Mg deposition induces structural deformation and alters the electronic properties of the complex. FeTPC forms different long-range ordered adsorbate structures on Ag(111). During annealing, the degradation of FeTPC occurs, with cyclodehydrogenation leading to the planarization of the ligands, as indicated by XPS and STM. In addition, the ligation of nitric oxide at the Fe center, resulting in significant changes in the electronic properties of the complex, was investigated. These findings highlight the tunability of corrole complexes for tailored applications in catalysis and materials science.

O 17.12 Mon 18:00 P2

**Theoretical investigation of 3,3”-dibromo-p-terphenyl on copper substrate** — ●Kevin Eberheim[1], Simone Sanna[1], Michael Dürr[2], and Mohit Jain[2] — [1]Institut für Theoretische Physik, Justus-Liebig-Universität Gießen, 35392 Gießen, Germany — [2]Institut for Applied Physics, Justus-Liebig-University Gießen, Germany

Chemoselectivity is a key parameter for building customized organic nanostructures via bottom-up approaches. Therefore, strategies are needed that allow connecting molecular entities at a specific stage of the assembly process in a chemoselective manner. Studying the mechanisms of such reactions is the key to apply these transformations for the buildup of organic nanostructures on surfaces. Especially, the knowledge about the precise adsorption geometry of intermediates at different stages during the reaction process and their interactions with surface atoms or adatoms is of fundamental importance, since often catalytic processes are involved. With first-principles simulations we can determine the adsorption geometry of the 3,3”-dibromo-p-terphenyl as well as adsorbed mono/diradicals and the halogens. For further comparability with experimental results simulations of Nudged Elastic Band (NEB) have been calculated for transitions between the observed linear chain and ring structures.