

Program Booklet

PriOSS Symposium
Schloss Rauischholzhausen
May 8th - 10th, 2023

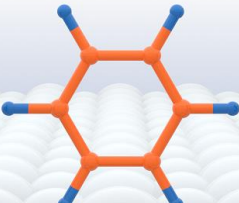
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Foto: Norbert Leipold, AFM: Daniel Martin-Jimenez

The construction of complex, functional molecules undoubtedly serves as a guiding vision for researchers in the field of nanosciences, not least since Feynman's famous statement "There is plenty of room at the bottom...". The atomic control of the molecular structure allows a direct influence on the properties of a material. In particular, functional materials on surfaces offer access to molecule-based functional devices such as graphene nanoribbons, which are already being used in prototype field-defect transistors. Other potential applications include quantum structures or topological insulators.

Since the deposition and positioning of molecular structures on surfaces for e.g. functional assemblies is difficult, nanostructures are nowadays increasingly successfully fabricated directly on surfaces; this is called "on-surface synthesis". This approach is of particular interest for two-dimensional (2D) materials, which per se require a surface as a support structure. The selective synthesis of such complex functional elements, however, still poses a particular challenge. While synthesis in solution can draw on almost 200 years of experience and perfected methods, the concepts of on-surface synthesis are still in their infancy. The two-dimensional (2D) nature of the surface opens up special opportunities to control reaction processes and offers to selectively build nanoarchitectures from atomic/molecular building blocks.

Our objective within the LOEWE focus group "PriOSS - Principles of On-Surface Synthesis" is to develop fundamental mechanistic models of surface-assisted synthesis and ultimately to create a new toolbox for this methodology, as it has existed for classical synthesis in solution for centuries. Therefore, we would like to bring together researchers with different expertise from the fields of physics, chemistry, and theory.

	Monday 08.05.2023	Tuesday 09.05.2023	Wednesday 10.05.2023
08:00		Breakfast	
08:30			
09:00		D. de Oteyza	L. Grill
09:30		P. Jelínek	F. Moresco
10:00		M. Lackinger	F. Albrecht
10:30		Coffee	Coffee
11:00	Registration	J. Repp	E. Meyer
11:30		R. Berndt	R. Tonner-Zech
12:00	Lunch	N. Doltsinis	M. Stöhr
12:30		Lunch	Closing Remarks
13:00			
13:30	S. Maier	Lunch	Lunch
14:00	D. Peña		
14:30	A. Studer	A. Schirmeisen	
		M. Dürr	
15:00	Coffee	H. A. Wegner	
		M. Gottfried	
15:30	P. Ruffieux	Coffee	
16:00	W. Auwärter	J. Sundermeyer	
		P. R. Schreiner	
16:30	R. Pérez	D. Mollenhauer	
		S. Sanna	
17:00	Posters	Posters	
17:30			
18:00			
18:30	Dinner	Dinner	
19:00			

PriOSS Symposium - Program

Schloss Rauschholzhausen – 8th-10th May, 2023

Monday, May 8, 2023

- 11:00-12:00** Registration
- 12:00-13:20** Lunch
- 13:20-13:30** Welcome
-
- 13:30-14:00** Bottom-up fabrication and electronic properties of planar π -extended cycloparaphenylene and non-planar carbon ribbons
Sabine Maier, Friedrich-Alexander University Erlangen-Nürnberg, Germany
- 14:00-14:30** Merging Organic Chemistry with Surface Science: from Nanographene Characterization to Single-Molecule Reactions
Diego Peña, Universidade de Santiago de Compostela, Spain
- 14:30-15:00** Novel On-Surface Transformations
Arvido Studer, University of Münster, Germany
- 15:00-15:30** Coffee Break
- 15:30-16:00** On-surface synthesis of nanographene spin clusters and chains
Pascal Ruffieux, Swiss Federal Laboratories for Materials Science and Technology, Dübendorf, Switzerland
- 16:00-16:30** On-Surface Reactions with Porphyrins
Willi Auwärter, Technical University of Munich, Germany
- 16:30-17:00** Molecular identification with AFM images and deep learning
Rubén Pérez, Universidad Autónoma de Madrid, Spain
- 17:00-18:30** Poster Session 1
- 18:30-20:00** Dinner

Tuesday, May 9, 2023

- 08:00-09:00** Breakfast
- 09:00-09:30** Circumventing the Stability Problems of Graphene Nanoribbon Zigzag Edges
Dimas G. de Oteyza, Donostia International Physics Center, San Sebastián, Spain
- 09:30-10:00** On-surface synthesis: what does it make it special?
Pavel Jelínek, Czech Academy of Sciences, Prague, Czech Republic
- 10:00-10:30** On-surface synthesis on inert and (partially) passivated substrates
Markus Lackinger, Technical University of Munich, Germany
- 10:30-11:00** Coffee Break
- 11:00-11:30** Single-molecule characterization in absence of conductance
Jascha Repp, University of Regensburg, Germany
- 11:30-12:00** Molecules on a Superconductor: Inducing Magnetism and Resonance-Enhanced Vibrational Spectroscopy
Richard Berndt, University of Kiel, Germany
- 12:00-12:30** N-heterocyclic carbenes for the functionalization of metal surfaces
Nikos Doltsinis, University of Münster, Germany
- 12:30-14:00** Lunch Break
- 14:00-14:30** Advances in Organic 2D Crystals - From On-Water Surface Chemistry to Functional Applications
Xinliang Feng, Technical University of Dresden, Germany
- 14:30-14:45** On-Surface Synthesis of Organic Molecular Structures: SPM enabled Strategies
André Schirmeisen, Justus Liebig University Gießen, Germany

- 14:45-15:00** Towards the third dimension: Organic molecular architectures synthesized on solid surfaces by means of solution-based click chemistry
Michael Dürr, Justus Liebig University Gießen, Germany
- 15:00-15:15** Systematic Studies towards Understanding of On-Surface Organic Chemistry – Dehydrogenative C–C Bond Formation
Hermann A. Wegner, Justus Liebig University Gießen, Germany
- 15:15-15:30** Beyond Graphene: On-Surface Synthesis Unlocks New Carbon Allotropes
J. Michael Gottfried, University of Marburg, Germany
- 15:30-16:00** Coffee Break
- 16:00-16:15** Unprecedented Conjugated Carbon and Carbon-Nitrogen Polymers, Rings, and Ribbons via Hybrid Solution & On-Surface Synthesis
Jörg Sundermeyer, University of Marburg, Germany
- 16:15-16:30** On-Surface Synthesis and Visualization of Aromatic P_3N_3
Peter R. Schreiner, Justus Liebig University Gießen, Germany
- 16:30-16:45** Theoretical Studies of the Mechanism of Ullmann Coupling of Naphthyl Halogen Derivatives to Binaphthyl on Coinage Metals
Doreen Mollenhauer, Justus Liebig University Gießen, Germany
- 16:45-17:00** Optical activation of surface localized phonon modes: A new path to enhanced catalytic activity?
Simone Sanna, Justus Liebig University Gießen, Germany
- 17:00-18:30** Poster Session 2
- 18:30-20:00** Dinner

Wednesday, May 10, 2023

- 08:00-09:00** Breakfast
- 09:00-09:30** Single-Molecule Motion at Surfaces: From Controlled Diffusion to Molecular Motors
Leonhard Grill, University of Graz, Austria
- 09:30-10:00** Tuning the mechanical properties of single molecules by on-surface reactions
Francesca Moresco, Technical University of Dresden, Germany
- 10:00-10:30** Selectivity in single-molecule reactions by tip-induced redox chemistry
Florian Albrecht, IBM Research-Zurich, Switzerland
- 10:30-11:00** Coffee Break
- 11:00-11:30** Mechanical Properties of Molecular Networks
Ernst Meyer, University of Basel, Switzerland
- 11:30-12:00** Bonding and Reactivity on Surfaces: From Fundamentals to Application with Computational Approaches
Ralf Tonner-Zech, University of Leipzig, Germany
- 12:00-12:30** 1D metal-coordinated polymers vs. graphene nanoribbons: influence of chirality and substrate
Meike Stöhr, University of Groningen, The Netherlands
- 12:30-14:00** Closing Remarks and Lunch

Poster Session 1

Monday, May 8, 17:00-18:30

- P 01** Ullmann coupling reactions on gold nanoparticles
Nathaniel Ukah, Justus Liebig University Gießen, Germany
- P 02** Towards Synthesis of Two-Dimensional Polymers on Metals by Photopolymerization
Lukas Grossmann, Technical University of Munich, Germany
- P 03** Mechanistic Insights into On-Surface Cyclization Reactions
Daniel Kohrs, Justus Liebig University Gießen, Germany
- P 04** Screening Non-alternant π -Electron Systems for Metal-Organic Interfaces: Interplay between Topology, Aromaticity, and Adsorption Behavior
Jakob Schramm, University of Leipzig, Germany
- P 05** Assigning the absolute configuration of Laurentstrich-4-ol
Kai Feuer, Justus Liebig University Gießen, Germany
- P 06** On-surface synthesis and characterization of [19]-starphene
Sergio Salaverría, Nanomaterials and Nanotechnology Research Center, El Entrego, Spain
- P 07** Adsorption, intermediate formation, and Ullmann coupling of p-terphenyl molecules on Cu(111): influence of the substitution pattern on the final reaction products on the surface
Mohit Jain, Justus Liebig University Gießen, Germany
- P 08** On the surface reaction of AzaTrux molecules on Au (111)
Outhmane Chahib, University of Basel, Switzerland
- P 09** Adsorption and mobility of tetracene on coinage metal substrates
Kevin Eberheim, Justus Liebig University Gießen, Germany
- P 10** On-Surface Synthesis of Non-Alternant Nanographenes
Lukas Heuplick, University of Marburg, Germany
- P 11** Chemical Bond Imaging of the On-surface Synthesis of Non-Alternant Carbon Nanoarchitectures
Miguel Wiche, Justus Liebig University Gießen, Germany

Poster Session 2

Tuesday, May 9, 17:00-18:30

- P 12** Synthesis of Arene-Fused Cyclooctenes and Cyclooctadienes *via* Bidentate Lewis Acid-Catalyzed Inverse Electron-Demand Diels-Alder Reaction for On-Surface Studies
Michel Große, Justus Liebig University Gießen, Germany
- P 13** Building up atomically-precise topological heterostructures in one-dimensional conjugated polymers
Bruno de la Torre, Czech Academy of Sciences, Prague, Czech Republic
- P 14** On-surface Synthesis and Characterization of Tridecacene
Zilin Ruan, University of Marburg, Germany
- P 15** STM-induced ring closure of vinylheptafulvene molecular dipole switches on Au(111)
Kwan Ho Au-Yeung, Technical University of Dresden, Germany
- P 16** On-Surface Synthesis of Kekulene and Isokekulene
Tim Naumann, University of Marburg, Germany
- P 17** Energy transfer-induced fluorescence of a non-fluorescent molecule
Tzu-Chao Hung, University of Regensburg, Germany
- P 18** Theoretical Studies on the Formation of Porous Carbon Nitrogen 2D Networks Derived from Tricyanobenzene and Tricyanotriazine on Coinage Metal Surfaces
Lara Alix Kaczmarek, Justus Liebig University Gießen, Germany
- P 19** AFM and STM combined study of thiahelicene on Cu(111)
Gema Navarro, University of Basel, Switzerland
- P 20** On-Surface Synthesis and Real-Space Visualization of Aromatic P₃N₃
Artur Mardyukov, Justus Liebig University Gießen, Germany
- P 21** On-Surface Metalation and Demetalation of Tetrapyrroles
Cong Guo and Jan Herritsch, University of Marburg, Germany

PriOSS Symposium
Talk Abstracts

Bottom-up fabrication and electronic properties of planar π -extended cycloparaphenylene and non-planar carbon ribbons

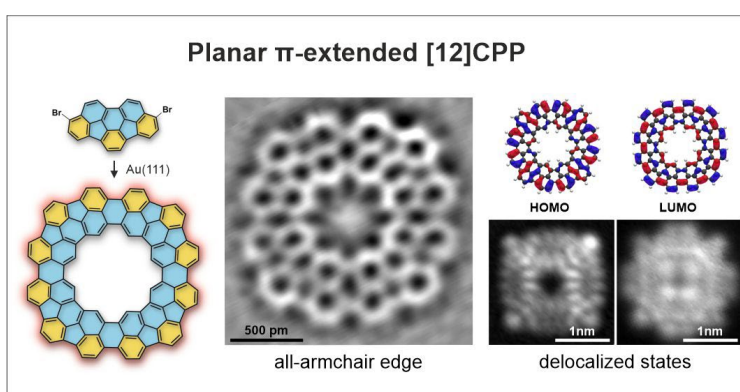
Sabine Maier

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On-surface synthesis via covalent coupling of adsorbed molecules on metal surfaces has attracted significant attention recently due to its potential to fabricate low-dimensional carbon materials with atomic precision. The bottom-up, atomically precise synthesis of carbon nanostructures enables the tailoring of their electronic properties at a molecular level. To understand and control the surface-chemistry-driven synthesis, many efforts have been made to design innovative precursors, explore novel reaction schemes, and utilize templating effects from the substrate.

My presentation focuses on high-resolution scanning probe microscopy experiments combined with density functional theory to demonstrate recent highlights on the assembly of surface-supported low-dimensional carbon structures. First, the assembly and electronic structure of planar π -extended cycloparaphenylene macrocycles, which represent the first nanographene with an all-armchair edge topology, will be presented [1]. [n]cycloparaphenylenes ([n]CPPs) have attracted significant attention due to their unique cyclic structure and highly effective para-conjugation leading to a myriad of fascinating (opto-)electronic properties. However, their strained topology prevents the π -extension of CPPs from converting them either into armchair nanobelts or planarized CPP macrocycles. We have successfully tackled this long-standing challenge and present the bottom-up synthesis and characterization of atomically precise in-plane π -extended [12]CPP on Au(111). The second part will discuss the bottom-up synthesis of covalently-linked non-planar carbon ribbons and their electronic properties depending on their adsorption geometry.



[1] F. Xiang, et al. *Nature Chem.*, 2022 14, 871–876.

Merging Organic Chemistry with Surface Science: from Nanographene Characterization to Single-Molecule Reactions

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The development of atomic force microscopy (AFM) and scanning tunnelling microscopy (STM) with functionalized tips has allowed the visualization of molecules adsorbed on different surfaces with submolecular resolution. This breakthrough, together with the possibility of inducing on-surface chemical reactions with the tip of the microscope, opens exciting applications of AFM/STM in chemistry and materials science.^[1]

Our group at CiQUS is specialized on the synthesis of large aromatic molecules. In this lecture I will illustrate the great potential of combining synthetic organic chemistry with surface science, by summarizing selected projects which were developed in close collaboration with groups specialised in AFM/STM. In particular, I will focus on the generation of elusive molecules (e.g. large acenes and triangulene derivatives),^[2-3] the introduction of new on-surface reactions (e.g. Diels-Alder cycloaddition),^[4] the synthesis of graphene materials (e.g. nanoporous graphenes),^[5] and the study of single-molecule reactions.^[6]

[1] L. Gross, B. Schuler, N. Pavliček, S. Fatayer, Z. Majzik, N. Moll, D. Peña and G. Meyer, *Angew. Chem. Int. Ed.* **57**, 3888 (2018).

[2] J. Krüger, F. García, F. Eisenhut, D. Skidin, J. M. Alonso, E. Guitián, D. Pérez, G. Cuniberti, F. Moresco, D. Peña *Angew. Chem. Int. Ed.* **56**, 11945 (2017).

[3] J. Hieulle, S. Castro, N. Friedrich, A. Vegliante, F. Romero Lara, S. Sanz, D. Rey, M. Corso, T. Frederiksen, J. I. Pascual, D. Peña *Angew. Chem. Int. Ed.* **60**, 25224 (2021).

[4] J. Castro-Esteban, F. Albrecht, S. Fatayer, D. Pérez, L. Gross, D. Peña **60**, 26346 (2021).

[5] C. Moreno, M. Vilas-Varela, B. Kretz, A. García-Leuke, M. V. Costache, M. Paradinas, M. Panighel, G. Ceballos, S. O. Valenzuela, D. Peña, A. Mugarza *Science* **360**, 199 (2018).

[6] F. Albrecht, S. Fatayer, I. Pozo, I. Tavernelli, J. Repp, D. Peña, L. Gross *Science* **377**, 298 (2022).

Novel On-Surface Transformations

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On-Surface Chemistry has attracted great attention as a bottom-up strategy for the synthesis of two-dimensional materials with interesting properties and functions. Various organic reactions have already been realized on metal surfaces.^[1-4]

In the lecture, on-surface reactions that have been developed in our laboratory in close collaboration with Prof. Harald Fuchs will be presented. The Glaser coupling^[2] is undoubtedly one of the most valuable on-surface reactions for the preparation of extended one- or two-dimensional π -systems. In the presentation, the thermal and also the photochemical Glaser coupling will be addressed. Further, the decarboxylative Glaser coupling, which was recently introduced by us having advantages over the classical thermal variant, will be discussed in the lecture (Figure 1). Silyl groups that are commonly used in solution phase chemistry can also be applied as protecting groups to on-surface synthesis. Moreover, appropriately substituted silanes can be activated on-surface and the activated Si-compounds then be used for the construction of π -extended systems that are linked through formal Si-Si double bonds.

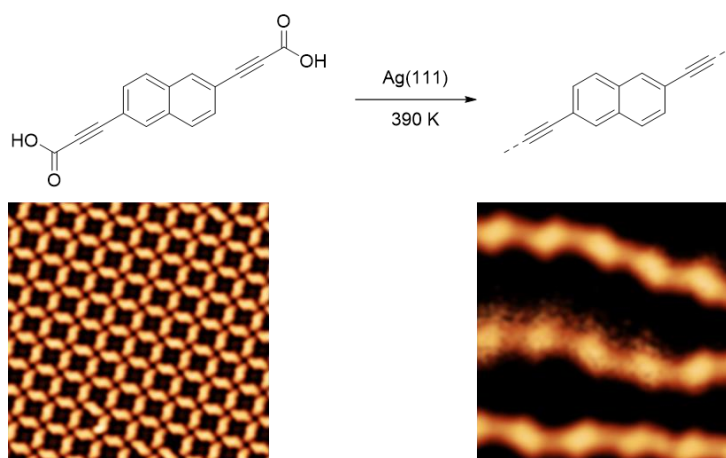


Figure 1: Reaction equation of the decarboxylative Glaser coupling of an aryl propiolic acid and STM images of the nanostructures on Ag(111) before and after the reaction.

Selected reviews:

- [1] Q. Shen, H. Y. Gao and H. Fuchs, *Nano Today*. **13**, 77 (2017).
- [2] P. A. Held, H. Fuchs and A. Studer, *Chem. Eur. J.* **23**, 5874 (2017).
- [3] T. Wang and J. Zhu, *Surf. Sci. Rep.* **74**, 97 (2019).
- [4] S. Clair and D. G. de Oteyza, *Chem. Rev.* **119**, 4717 (2019).

On-surface synthesis of nanographene spin clusters and chains

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Recent progress in the on-surface synthesis of nanographenes has given access to an extremely rich materials class where physical properties can be tuned in a wide range. The most prominent nanographenes include armchair graphene nanoribbons (GNRs) with width-dependent electronic band gaps [1], zigzag GNRs with spin-polarized edge states [2] and width-modulated GNRs hosting tunable topological bands [3]. Most recently, the successful synthesis of a series of open-shell nanographenes with magnetically nontrivial ground states has catapulted carbon-based magnetism to a new level. The basic concept followed here is the realization of sublattice-imbalanced or topologically frustrated nanographenes that host unpaired electrons. A deterministic realization of such nanographenes is achieved through the combined solution and on-surface synthesis approach.

Here, I will give an overview on how on-surface synthesis gives access to precise tuning of exchange coupling by chemical design and realize a series of prototypical magnetic building blocks [4] allowing realization of pure carbon spin chains with specific symmetry-protected topological phases [5]. In order to fully explore the properties of the nanographene-based spin clusters and chains, activation and passivation of specific spin sites is of ultimate importance. Related strategies using the scanning probe tip-based control will be introduced and applied to manipulate length and the topological phase of nanographene spin chains.

References:

- [1] J. Cai, P. Ruffieux, R. Jaafar, M. Bieri, T. Braun, S. Blankenburg, M. Muoth, A. P. Seitsonen, M. Saleh, X. Feng, K. Muellen, and R. Fasel, *Nature* **466**, 470 (2010).
- [2] P. Ruffieux, S. Wang, B. Yang, C. Sánchez-Sánchez, J. Liu, T. Dienel, L. Talirz, P. Shinde, C. A. Pignedoli, D. Passerone, T. Dumslaff, X. Feng, K. Müllen, and R. Fasel, *Nature* **531**, 489 (2016).
- [3] O. Gröning, S. Wang, X. Yao, C. A. Pignedoli, G. Borin Barin, C. Daniels, A. Cupo, V. Meunier, X. Feng, A. Narita, K. Mullen, P. Ruffieux, and R. Fasel, *Nature* **560**, 209 (2018).
- [4] E. Turco, A. Bernhardt, N. Krane, L. Valenta, R. Fasel, M. Juríček, and P. Ruffieux, *JACS Au* jacsau.2c00666 (2023).
- [5] S. Mishra, G. Catarina, F. Wu, R. Ortiz, D. Jacob, K. Eimre, J. Ma, C. A. Pignedoli, X. Feng, P. Ruffieux, J. Fernández-Rossier, and R. Fasel, *Nature* **598**, 287 (2021).

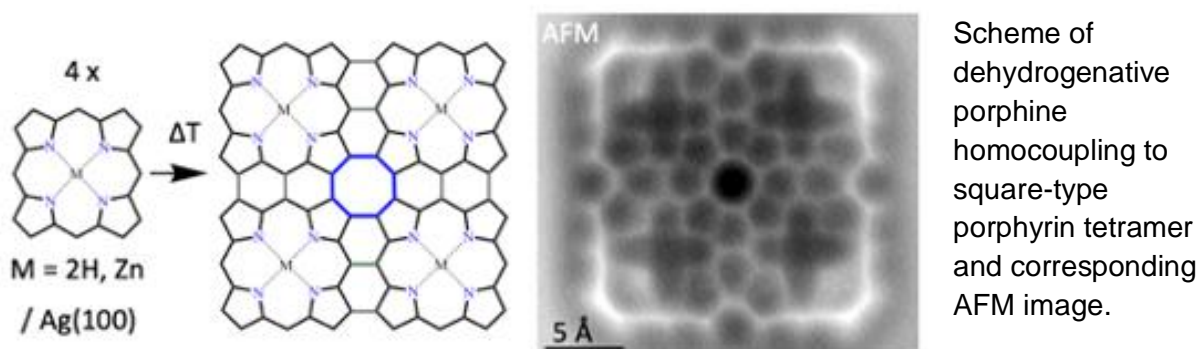
On-Surface Reactions with Porphyrins

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On-surface chemistry protocols on metal supports provide elegant routes to individual molecular complexes, oligomers, and advanced architectures with distinct physical, chemical and structural properties [1,2]. In this context, porphyrins and other tetrapyrroles represent versatile precursors that can undergo metalation, ring-opening, and ring-closing reactions.

In my presentation, I will start with a brief overview on our research efforts towards surface supported two-dimensional materials and distinct molecular nanostructures in ultrahigh vacuum. The main part of the talk will then focus on the formation of porphyrin-based products on single crystalline Ag and Au surfaces by temperature-induced ring-closing reactions. Specifically, distinct oligomers including square-type porphyrin tetramers featuring a planar, central antiaromatic cyclooctatetraene (COT) moiety will be discussed. These tetramers were prepared on Ag(100) by dehydrogenative homocoupling employing unsubstituted Zn- and free-base porphines (see Figure) as precursors [3]. Furthermore, the synthesis of π -extended oxygen-embedded porphyrins via O-annulation on Au(111) will be addressed, yielding high selectivity and yield for planar porphyrin products with distinct symmetries and oxygen content, which are not easily achieved by solution chemistry. Low-temperature scanning tunnelling microscopy (STM), spectroscopy (STS), and bond-resolved atomic force microscopy (AFM) supported by complementary theoretical modelling were used to comprehensively characterize chemical structure and electronic properties of the square-type tetramers and O-doped porphyrins. These studies thus give access, and insights, to novel porphyrinoids with distinct properties on metal supports.



Scheme of dehydrogenative porphine homocoupling to square-type porphyrin tetramer and corresponding AFM image.

[1] L. Grill, S. Hecht, *Nat. Chem.* **12**, 115 (2020)

[2] R.S.K. Houtsmā, J. de la Rie, M. Stöhr, *Chem. Soc. Rev.* **50**, 6541 (2021)

[3] E. Corral Rascon *et al.*, *J. Am. Chem. Soc.* **145**, 967 (2023)

Molecular identification with AFM images and deep learning

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High resolution non-contact atomic force microscopy (HR-AFM) with CO-functionalized metal tips reveals the internal structure of adsorbed organic molecules with unprecedented resolution. resolving intermolecular features, determining bond orders, and characterizing intermediates and final products generated in on-surface reactions [1]. Recent advances in the interpretation of the AFM contrast observed in porphycenes [2] and on self-assembled molecular layers driven by either halogen [3] or hydrogen bonds [4], shows that there are clear connections between fundamental chemical properties of the molecules and key features imprinted in force images with submolecular resolution.

Inspired by these results, we address the problem of the complete identification (structure and composition) of molecular systems solely based on AFM images, without any prior information, exploiting deep learning (DL) techniques. In a first step, we restrict ourselves to a small set of 60 flat molecules and demonstrate the automatic classification of AFM experimental images by a DL model trained essentially with a theoretically generated data set [5]. We analyze the limitations of two standard models for pattern recognition when applied to AFM image classification and develop a model with the optimal depth to provide accurate results and to retain the ability to generalize. We show that a variational autoencoder (VAE) provides a very efficient way to incorporate into the training set, from very few experimental images, characteristic features that assure a high accuracy in the classification of both theoretical and experimental images.

Learning from the successes and the limitations of this proof-of-concept, we have developed QUAM-AFM, the largest data set of simulated AFM images generated from a selection of 685,513 molecules that span the most relevant bonding structures and chemical species in organic chemistry [6]. QUAM-AFM contains, for each molecule, 24 3D image stacks, each consisting of constant-height images simulated for 10 tip-sample distances with a different combination of AFM operational parameters, resulting in a total of 165 million images. The data provided for each molecule includes, besides a set of AFM images, ball-and-stick depictions, IUPAC names, chemical formulas, atomic coordinates, and map of atom heights. In order to simplify the use of the collection as a source of information, we have developed a graphical user interface that allows the search for structures by CID number, IUPAC name, or chemical formula. Using QUAM-AFM, we have designed and trained different deep learning models to go beyond the classification of limited groups of molecules and achieve the complete identification of an arbitrarily complex, unknown molecule, including multimodal recurrent networks (M-RNNs) [7] and Conditional Generative Adversarial Networks (CGANs) [8].

[1] L. Gross, et al., *Angew. Chem.Int. Ed.* **57**, 3888 (2018)

[2] T. K. Shimizu, et al., *J. Phys. Chem. C* **124**, 26759 (2020)

[3] J. Tschakert, et al., *Nat. Commun.* **11**, 5630 (2020)

[4] P. Zahl, et al. *Nanoscale* **13**, 18473 (2021)

[5] J. Carracedo-Cosme, et al., *Nanomaterials* **11**, 1658 (2021)

[6] J. Carracedo-Cosme, et al., *J. Chem. Inf. Model.* **62**, 1214 (2022)

[6] J. Carracedo-Cosme, et al., *ACS Appl. Mater. Interfaces* (2023) 10.1021/acsami.3c01550

[7] J. Carracedo-Cosme and R. Perez, (2023) submitted (10.48550/arXiv.2205.00447)

Circumventing the Stability Problems of Graphene Nanoribbon Zigzag Edges

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Carbon nanostructures with zigzag edges exhibit unique properties with exciting potential applications. Such nanostructures are generally synthesized under vacuum because their zigzag edges are unstable under ambient conditions [1]: a barrier that must be surmounted to achieve their scalable exploitation. Here, we prove the viability of chemical protection/deprotection strategies for this aim, demonstrated on labile chiral graphene nanoribbons (chGNRs) [2]. Upon hydrogenation, the chGNRs survive an exposure to air, after which they are easily converted back to their original structure *via* annealing (Fig. 1). We also approach the problem from another angle by synthesizing a chemically stable oxidized form of the chGNRs that can be converted to the pristine hydrocarbon form *via* hydrogenation and annealing. These findings may represent an important step toward the integration of zigzag-edged nanostructures in devices. Lastly, we also study the magnetism associated to remaining defects, as well as the dependence of the magnetic interactions on structural details [3].

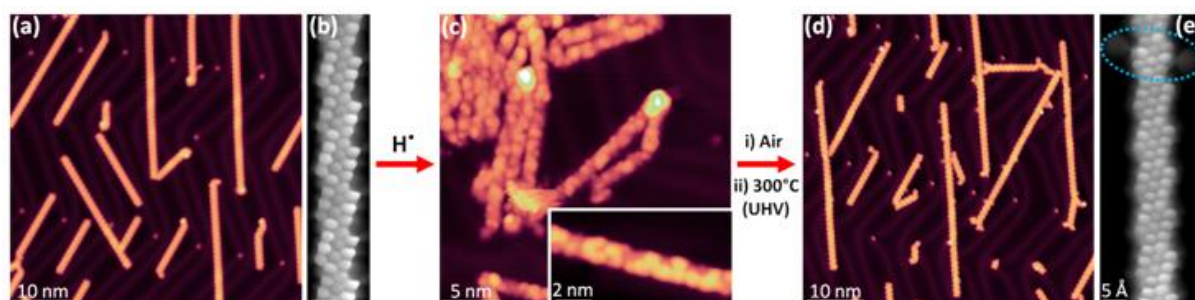


Fig 1. STM image of a pristine (3,1)-chGNRs sample on Au(111) (a) with an associated bond-resolving image (b); after exposure to atomic hydrogen (c); and the same sample after air exposure and annealing (d), along with another bond resolving image (e).

[1] A. Berdonces-Layunta, et al., Chemical Stability of (3,1)-Chiral Graphene Nanoribbons, ACS Nano **2021**, 15, 5610–5617

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On-surface synthesis: what does it make it special?

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The recent progress in on-surface synthesis enabled the formation of new molecular structures, which are not available in traditional organic chemistry in solution [1]. In this talk, we will present several examples demonstrating the outstanding capabilities of on-surface synthesis. We will combine experimental measurements with theoretical analysis based on quantum mechanics/molecular mechanics (QM/MM) methods. This combination provides a detailed insight into the mechanism of chemical reactions, which enables us to identify important factors playing a role in on-surface synthesis. These factors will help to identify why on-surface chemistry enables the synthesis of molecules that cannot be achieved by traditional methods of organic synthesis. Namely, we will discuss the influence of surface 2D confinement [2], the role of metallic adatoms [3,4], as well as the importance of internal vibrational models [5] in on-surface chemical synthesis.

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On-surface synthesis on inert and (partially) passivated substrates

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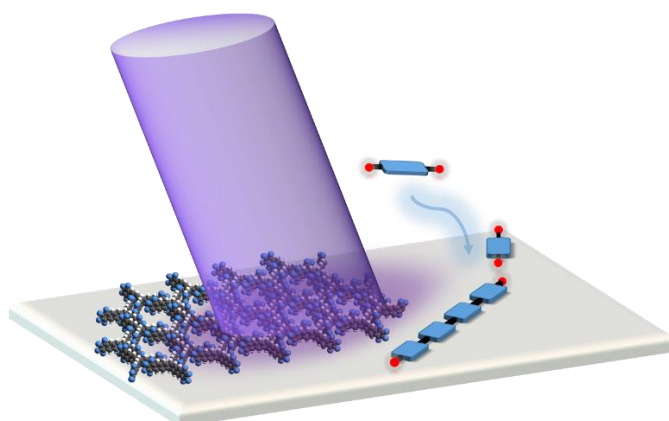
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On-surface synthesis is most often performed on metal surfaces. Their chemically active role is required to lower activation barriers so that the reaction can proceed at temperatures low enough to prevent loss of reactants by desorption. However, the metal surfaces exert an undesirably strong influence on the adsorbed covalent nanostructures, which also affects their (opto-)electronic properties to the point where functionality is compromised. This could be a major obstacle for future applications.

Although reversible condensation reactions are well established on inert graphite surfaces, carbon-carbon coupling remains largely elusive. We introduce and discuss several concepts that enable synthesis on less reactive to completely inert surfaces,[1] namely photochemical coupling,[2],[3] synthesis on partially passivated metal surfaces, and activation of molecular building blocks prior to their deposition.[4]

We obtained two-dimensional polymers ordered at the mesoscale by topochemical photopolymerization of a fluorinated anthracene-triptycene monomer on graphite surfaces.[3] To achieve self-assembly into a photopolymerizable monolayer packing, crystal engineering was required and achieved by passivating the graphite surface with an alkane monolayer.

Covalent coupling of 4,4"-diiodo-*p*-terphenyl precursors to extended *para*-poly-phenylene (PPP) wires was achieved on iodine-passivated metal surfaces by direct deposition of terphenyl biradicals.[4] These were generated en route in a dedicated radical deposition source that facilitates the spatiotemporal separation of monomer activation and subsequent covalent coupling. Lastly, we show that partially passivated surfaces with attenuated reactivity can yield covalent nanostructures that cannot be obtained directly on metal surfaces.



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Single-molecule characterization in absence of conductance

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Scanning probe microscopy (SPM) has revolutionized our understanding of the atomistic world. We introduce a novel variant of SPM by combining principles of STM and atomic force microscopy (AFM) enabling electronic characterization in absence of sample conductance. Further, this method provides access to intermediate timescales that are relevant for spin manipulation and relaxations.

Instead of the usual direct current in conventional STM, we drive a tiny alternating current between the microscope's tip and a single molecule under study. Thereby, we can access out-of-equilibrium charge states that are out of reach for conventional STM [1]. Extending this technique by electronic pump-probe spectroscopy [2], see Fig. 1, we measured the triplet lifetime of an individual pentacene molecule and lifetime quenching by nearby oxygen molecules [3]. By means of single-molecule manipulation techniques, different arrangements with oxygen molecules were created and characterized with atomic precision, allowing for the direct correlation of molecular arrangements with the lifetime of the quenched triplet.

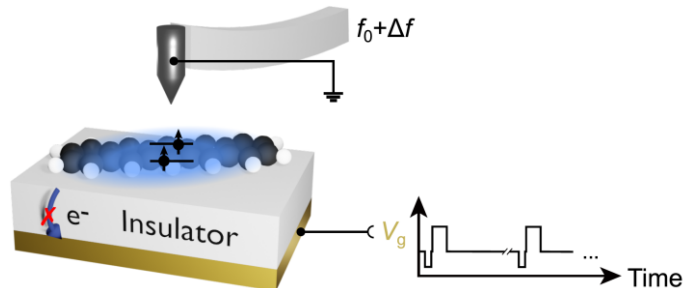


Fig. 1: Schematic of the setup, by which we probe the triplet lifetime of an individual pentacene molecule. The molecule is placed on an insulator preventing any electron exchange with the substrate. By means of voltage pulses we bring the molecule into its triplet state and probe how fast the triplet decays.

Combining the triplet-lifetime measurements with radio-frequency magnetic-field driving we further introduce AFM-based electron spin resonance. We demonstrate such ESR detection of electron spin transitions between the non-equilibrium triplet states of individual pentacene molecules. Spectra of these transitions exhibit sub-nanoelectronvolt energy resolution, allowing local discrimination of molecules that only differ in their isotopic configuration. Furthermore, the electron spins can be coherently manipulated over tens of microseconds, likely not limited by the detection method but by the molecular properties [4].

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Molecules on a Superconductor: Inducing Magnetism and Resonance-Enhanced Vibrational Spectroscopy

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Magnetic impurities can induce so-called Yu-Shiba-Rusinov (YSR) resonances in the energy gap of a superconductor. We use these resonances for spin detection in a scanning tunneling microscope and demonstrate that diamagnetic phthalocyanine molecules acquire a spin when they are arranged into supramolecular arrays on superconducting Pb(100). Spectroscopy and modeling reveal that the electrostatic fields of its neighbors render a molecule paramagnetic.

Inelastic tunneling spectroscopy of vibrational excitations usually suffers from low sensitivity and limited spectral resolution. We harness YSR resonances to enhance the inelastic signal by more than an order of magnitude and to improve the energy resolution beyond the thermal broadening limit. The method may help to further probe the interaction of molecules with their environment and to better understand selection rules for vibrational excitations.

Finally, some data on self-assembled spin-crossover complexes may be presented.

Work done in collaboration with Jan Homberg, Alexander Weismann, Manuel Gruber, Troels Markussen, Sven Johannsen, Sascha Schüddekopf, Sascha Ossinger, Jan Grunwald, Alexander Herman, Heiko Wende, Felix Tuczek.

N-heterocyclic carbenes for the functionalization of metal surfaces

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N-heterocyclic carbenes (NHCs) with suitable side groups exhibit the unique property of binding strongly to coinage metal surfaces via a single covalent bond whilst maintaining a high lateral mobility. Ab initio molecular dynamics simulations have revealed that the origin for this behaviour lies in the fact that such NHCs pull out a metal atom from the surface which then serves as a vehicle for NHC migration across the surface [1]. NHCs thus offer a promising alternative to thiol-based ligands for the formation of self-assembled monolayers.

For other applications, such as molecular rotors, it is desirable to anchor the NHCs at a fixed position on the surface. A unidirectionally rotating NHC species has been developed following theoretically derived design principles [2]. As a prerequisite it has an asymmetric rotational potential and can be driven by inelastic tunneling of electrons from an STM tip.

We have shown that surface functionalization with NHCs can drastically enhance the catalytic properties of Pd nanoparticles. Density functional theory calculations predict a substantial lowering of the bromobenzene activation barrier as a consequence of electron density being injected into the metal by the NHCs [3].

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Advances in Organic 2D Crystals — From On-Water Surface Chemistry to Functional Applications

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In contrast to the tremendous efforts dedicated to the exploration of graphene and inorganic 2D crystals such as metal dichalcogenides, boron nitride, black phosphorus, metal oxides, and nitrides, there has been much less development in organic 2D crystalline materials, including the bottom-up organic/polymer synthesis of graphene nanoribbons, 2D metal-organic frameworks, 2D polymers/supramolecular polymers, as well as the supramolecular approach to 2D organic nanostructures. One of the central chemical challenges is to realize a controlled polymerization in two distinct dimensions under thermodynamic/kinetic control in solution and at the surface/interface. In this talk, we will present our recent efforts in bottom-up synthetic approaches toward novel organic 2D crystals with structural control at the atomic/molecular level. On-water surface synthesis provides a powerful synthetic platform by exploiting surface confinement and enhanced chemical reactivity and selectivity. We will particularly present a surfactant-monolayer assisted interfacial synthesis (SMAIS) method that is highly efficient in promoting the programmable assembly of precursor monomers on the water surface and subsequent 2D polymerization in a controlled manner. 2D conjugated polymers and coordination polymers belong to such material classes. The unique 2D crystal structures with possible tailoring of conjugated building blocks and conjugation lengths, tunable pore sizes and thicknesses, as well as impressive electronic structures, make them highly promising for a range of applications in electronics, optoelectronics, and spintronics. Other physicochemical phenomena and application potential of organic 2D crystals, such as in membranes, will also be discussed.

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On-Surface Synthesis of Organic Molecular Structures: SPM enabled Strategies

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On-surface synthesis is at the verge of emerging as the method of choice for the generation and visualization of new molecules and molecular assemblies. In particular constructing low-dimensional covalent assemblies with tailored size and connectivity is challenging yet often key for applications in molecular electronics where optical and electronic properties of the quantum materials are highly structure dependent.

On strategy is high resolution imaging of organic molecules and nanoarchitectures before and after on-surface reactions took place, using atomic force microscopy with CO-tip functionalization. Recent examples include nanographene flakes and rings [1,2] as well as complex nanoribbon-allotropes [3]. Even systematic step-by-step observation of complete chemical reaction pathways is possible by repetitive imaging and surface annealing, often in combination with dedicated DFT calculations [4].

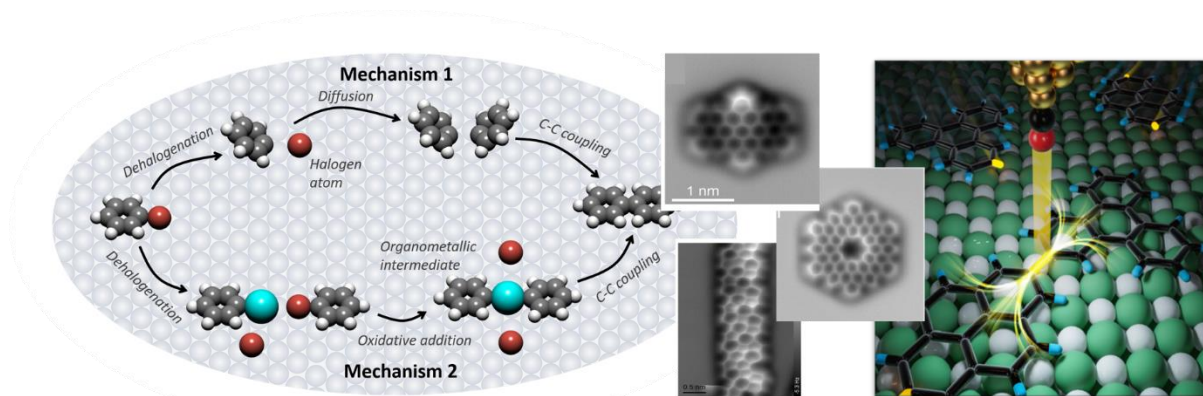


Figure 1: (left to right) Visualization of on-surface reaction pathways, examples of on-surface synthesized molecular structures [1,2,3], SPM construction of covalent assemblies [5]

The second approach is to build prototypical structures block by block using voltage pulse of an atomic force microscope tip, while tracking the structural changes with single-bond resolution [5]. Recently, we demonstrated fabrication of covalent homo-dimers in cis and trans configurations and homo-/hetero-trimers, that were selectively synthesized by a sequence of dehalogenation, translational manipulation and intermolecular coupling of halogenated precursors. Lastly, we achieved on-surface synthesis of the structurally elusive molecule P_3N_3 , an inorganic aromatic analogue of benzene, not obtainable via traditional synthetic methods [6]. Our work thus highlights strategies for synthesizing unique molecules as well as covalent nanoarchitectures, studying structural modifications and revealing pathways of intermolecular reactions.

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Towards the third dimension: Organic molecular architectures synthesized on solid surfaces by means of solution-based click chemistry

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In most on-surface reactions, the solid (metal) substrates act 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 including the combination of UHV- and solution-based surface chemistry have to be applied.

For the growth of 3D structures on silicon surfaces, we have followed both of these routes. Using a carefully tuned enolether/tetrazine cycloaddition, dimethyl 1,2,4,5-tetrazine-3,6-dicarboxylate molecules were coupled under UHV conditions to the enol ether group of a functionalized cyclooctyne which was adsorbed on the silicon (001) surface via the strained triple bond of cyclooctyne [1].

Here we show how to combine surface functionalization performed under UHV conditions with solution-based alkyne-azide click reactions (Fig. 1). The UHV-based functionalization of Si(001) was realized via chemoselective adsorption of ethynyl cyclopropyl cyclooctyne (ECCO) from the gas phase. The samples were then directly transferred from UHV into the reaction solution where alternating layers of bisazide and bisalkyne were coupled subsequently step by step without exposure to ambient conditions [2]. Two selective reaction schemes were employed, which ensured the controlled growth of organic structures perpendicular to the surface. Each reaction step was monitored by means of XPS in UHV and the selectivity of the reaction schemes in use was demonstrated.

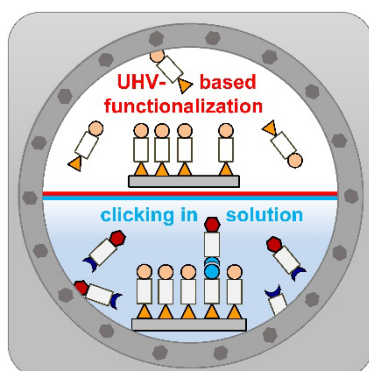


Fig. 1: Combination of UHV-based surface functionalization and solution-based, chemoselective click chemistry schemes was used to grow organic structures perpendicular to the surface of a solid substrate.

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Systematic Studies towards Understanding of On-Surface Organic Chemistry – Dehydrogenative C–C Bond Formation

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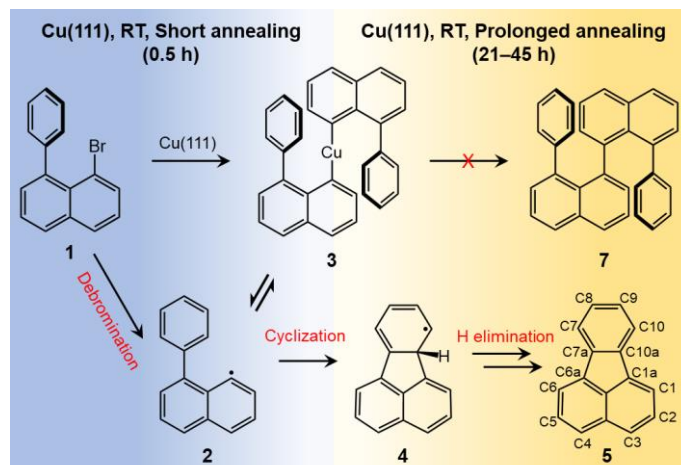
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While there has been over a century of experience in conducting organic chemical reactions in solution, the knowledge about the course of organic transformations on surfaces is still in its infancies. The establishment of guiding principles for synthesizing molecules selectively on surface would allow to create functional entities directly on a substrate providing an easy integration into devices.

In close collaboration with physics/microscopy and theory we aim to address parameters which control on-surface reactivity.[1-4] Key in these studies is the clever design of precursors to probe specific questions, such as reactivity of leaving groups or mobility on the surface depending on the structure.

Herein, a current study on the cyclization of phenylnaphthalene will be presented. Key is a dehydrogenative C–C bond formation. Using different precursors, the detailed mechanism of this elementary on-surface process has been elucidated. These insights will further enhance the tool box of on-surface reactions and serve as basis for the design of new transformations.



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Beyond Graphene: On-Surface Synthesis Unlocks New Carbon Allotropes

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The quest for planar sp^2 -hybridized carbon allotropes other than graphene, such as phagraphene and biphenylene network, has stimulated substantial research efforts because of the materials' predicted unique mechanical, electronic, and transport properties. However, their syntheses remain challenging due to the lack of reliable protocols for generating nonhexagonal rings during the in-plane tiling of carbon atoms. We have developed an on-surface synthesis strategy by which we first make straight polymer chains, which then link to form the nonbenzenoid graphene isomers. In this way, we synthesized biphenylene network with periodically arranged 4-6-8-membered rings, through an on-surface inter-polymer dehydrofluorination reaction (Fig. 1a). Biphenylene network is the only experimentally known planar sp^2 carbon so far, besides graphene. Its characterization by scanning probe methods reveals that it is metallic rather than a dielectric already at very small dimensions [1]. A complementary approach was used to generate phagraphene nanoribbons based on 5-6-7-membered rings (Fig. 1b). Here, we polymerized an azulene-based precursor containing the odd-numbered rings. Additional 4- and 7-membered rings can be formed during dehydrogenative C-C coupling of the intermediate polyazulene chains, resulting in tetra-penta-hepta(TPH)-graphene (Fig. 1c) with 4-5-7-membered rings and metallic properties [2].

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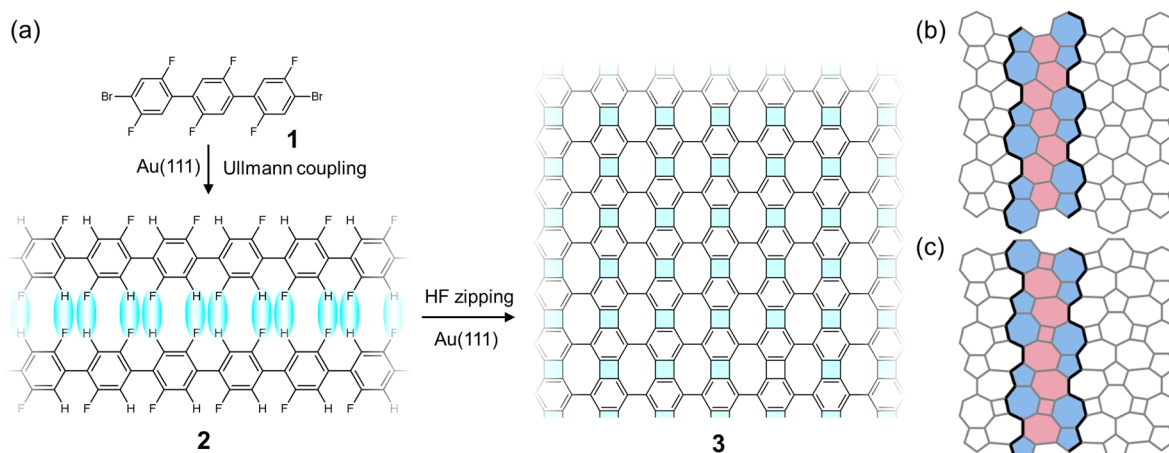


Figure 1. (a) On-surface synthesis of biphenylene network **3** from 4,4''-dibromo-2,2',2'',5,5',5''-hexafluoro-1,1':4',1''-terphenyl **1** by HF-zipping of the intermediate poly(p-phenylene) polymer **2**. (b) Phagraphene and (c) tetra-penta-hepta(TPH)-graphene.

Unprecedented Conjugated Carbon and Carbon-Nitrogen Polymers, Rings, and Ribbons via Hybrid Solution & On-Surface Synthesis

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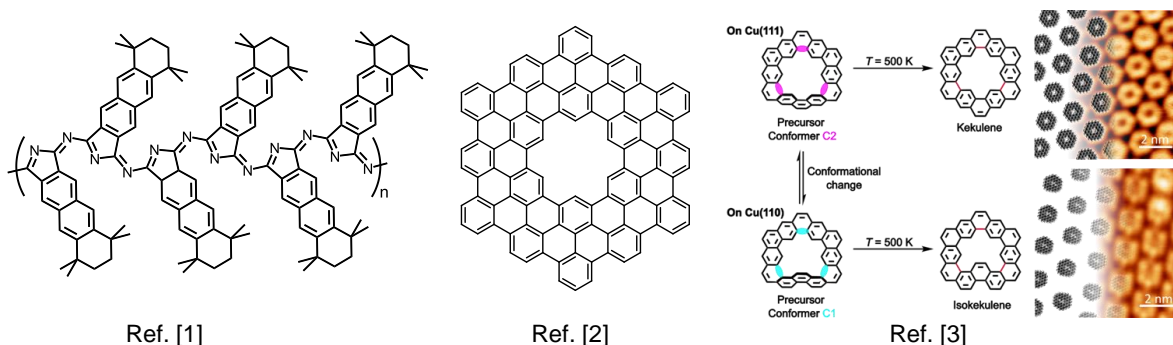
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We describe a series of novel on-surface generated polyaromatic molecules and polymers formed via a sequence of solution synthesis steps towards volatile precursors with a designed pattern of functional groups (Sundermeyer group), their UHV gas phase deposition as sub-monolayers on well-defined single crystalline metal surfaces and their temperature-controlled oligo- and polymerization or condensation towards unprecedented structural motives including their characterization (Gottfried, Ebeling and collaborators). The focus of this short talk will be on three facets: First, the gadolinium atom induced cyclo-pentamerization or catalytic polymerization of a designer naphthalene-1,2-dicarbonitrile towards an unprecedented supernaphthalocyanine and a polycyanine polymer displaying a unique alternating $[-C=N-]_n$ spine.[1] Our second example displays the on-surface synthesis of C108, a double-stranded hexagonal cycloarene containing 108 sp^2 carbon atoms [2] and a porous graphene nano-ribbon with a band gap tuned by regular pores within the ribbon scaffold. Finally the shortest synthesis of kekulene is demonstrated: four steps in solution, one on-surface.[3] To our surprise the selectivity of the final dehydrogenation step can be switched from kekulene towards unprecedented isokekulene by switching from Cu(111) to a Cu(110) catalytic surface.



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On-Surface Synthesis and Visualization of Aromatic P₃N₃

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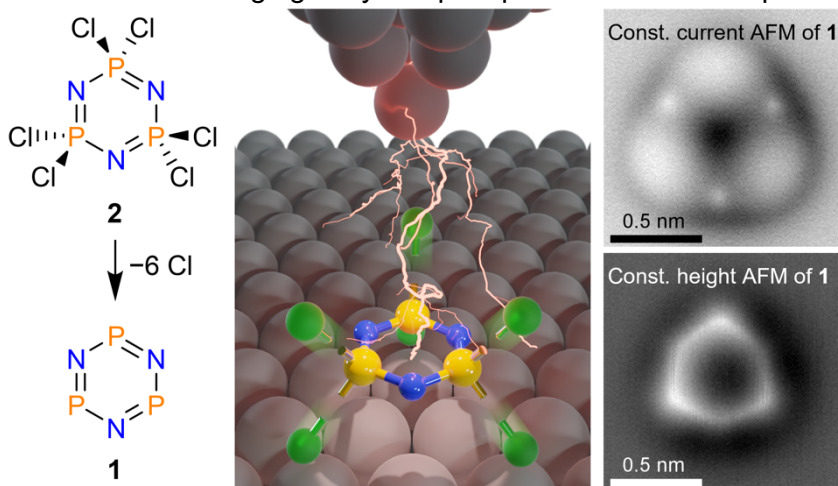
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“Seeing is believing”^[1] is a very human trait even though we know that our visual impressions cannot be fully trusted. Still, also in the molecular world, the visualization of atoms and molecules has begun to revolutionize not only the way we perceive and characterize but also how we make molecular structures. On-surface synthesis (OSS) by single-molecule imaging and manipulation^[2] has demonstrated its prowess recently with the preparation of, for instance, arynes,^[3] triangulene,^[4] and cyclo[18]carbon^[5] with the goal of making unusual molecular structures. Here we demonstrate that even fleetingly existing, highly reactive inorganic structures not accessible by conventional means can be prepared through OSS. At the same time, we remark that the mechanisms of on-surface reactivity are not yet well understood and possibly quite different from traditional synthetic approaches.^[6] It does, however, expand our arsenal of synthetic methods as we demonstrate with the synthesis of *D*_{3h}-symmetric cyclotriphosphazene (P₃N₃), an inorganic aromatic analogue of benzene. Here, we report the preparation of this fleetingly existing species on Cu(111) and Au(111) surfaces at 5.2 K through molecular manipulation with unprecedented precision, *i.e.*, voltage pulse-induced sextuple dechlorination of an ultra-small (about 6 Å) hexachlorophosphazene P₃N₃Cl₆ molecule by the tip of a scanning probe microscope. Real-space atomic-level imaging of cyclotriphosphazene reveals its planar *D*_{3h}-symmetric ring structure. Furthermore, this demasking strategy has been expanded to generate cyclotriphosphazene from a hexaazide precursor P₃N₂₁ via a different generation method (photolysis) for complementary measurements by matrix isolation infrared and ultra-violet spectroscopy.



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Theoretical Studies of the Mechanism of Ullmann Coupling of Naphthyl Halogen Derivatives to Binaphthyl on Coinage Metals

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Knowledge of the thermodynamics and kinetics of Ullmann coupling reactions to elucidate the overall reaction mechanism and the effects of the different surfaces and molecules is sparse and can be investigated by quantum chemical calculations.

Here we present the elucidation of the reaction mechanisms of several naphthalene halide derivatives on (111) coinage metal surfaces to binaphthalene using density functional theory with dispersion correction [1]. We compare the different reaction steps and overall reaction mechanism of single halogenated naphthalene with two halogens (Br, I) on the three different coin surfaces copper, silver and gold. As a result, we show that the qualitative order of the reaction barriers on the different catalytic surface metals is not the same for all reaction steps. Even the highly reactive copper surface inhibits certain reaction steps, such as the C-C coupling reaction. This is due to steric hindrance and the stability of the organometallic bond. The projected “Crystal Orbital Hamilton Populations” method [2] was used to analyse the covalent bond between metal surface and naphthyl radicals. Compared to copper and silver, the orbital overlap between the radical carbon atom and the binding gold atom was found to be surprisingly large. This effect has also been shown to influence the structure and reaction barriers in Ullmann coupling reactions [3].

Overall, we present detailed insights into the mechanism of surface Ullmann coupling reactions on coin metal surfaces, which will help in the design of novel precursors and the selection of favorable surface metals.

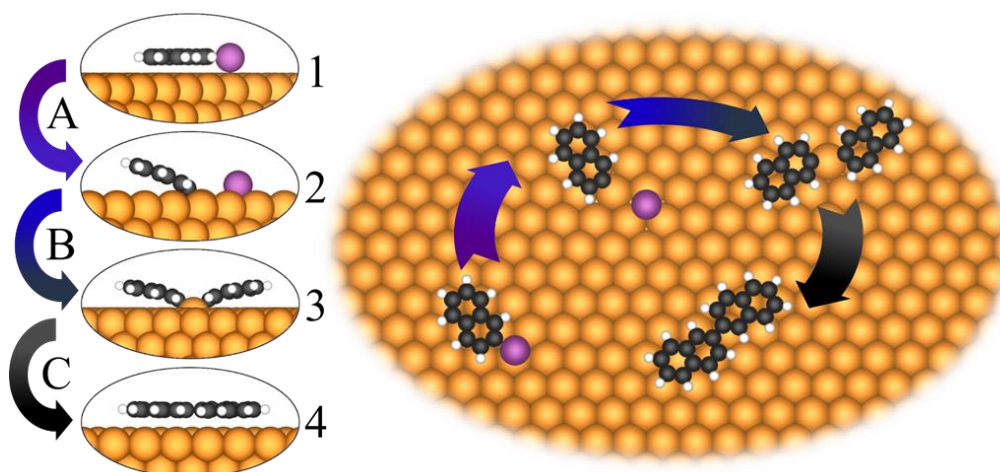


Figure 1: Schematic overview of the reaction steps of the on-surface Ullmann coupling mechanism demonstrated on 2-iodonaphthalene on a copper(111) surface.

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Optical activation of surface localized phonon modes: A new path to enhanced catalytic activity?

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Metal surfaces can act as reservoirs of charge carriers and thus facilitate chemical reactions. The catalytic activity of metal substrates can be further enhanced, provided the surface charge density can be manipulated. One possible way to control surface charges is the selective occupation of surface localized phonon modes, e.g., by optical activation. Unfortunately, most of the coinage metals crystallize in a Bravais lattice with a single atom in the unit cell and do not possess optical phonon modes. This notwithstanding, we report the first evidence of Raman scattering from surface phonons of a pristine metal surface [1]. Our study reveals a Raman-active surface vibrational resonance on Cu(110) with a surprisingly large scattering efficiency. With the incident photon energy close to the energy of the Cu(110) surface state electronic transition [2], the Raman scattering from the surface optical resonance can be significantly enhanced, while any contribution from bulk phonons is absent. Density functional theory calculations of the electronic band structure show that the observed Raman signal can be unambiguously attributed to the coupling of this specific mode with electronic surface states, and provide insight into the mechanism causing the strong enhancement of the Raman scattering.

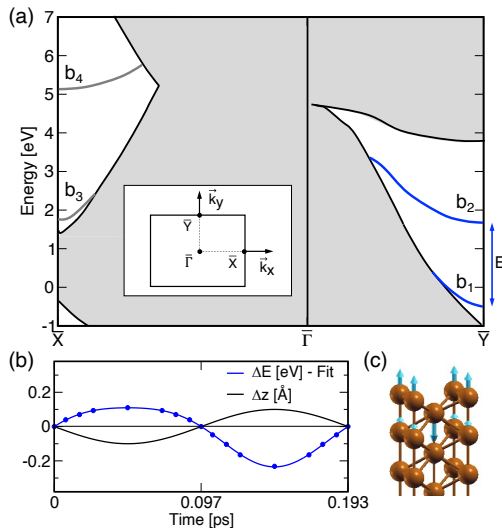


Figure 1: a) Calculated electronic band structure of Cu(110): Surface states are labeled b_i , while the surface-projected bulk bands are overlaid in gray. The inset shows the surface Brillouin zone with the high symmetry points used for the calculation. (b) Variation of the spacing of the upper two atomic planes of the Cu lattice (Δz) and resulting variation of the distance between b_1 and b_2 at \bar{Y} (ΔE), for a single oscillation period. The fit through the ΔE points serves as a guide to the eyes. (c) Vibrational pattern of the surface phonon resonance.

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Single-Molecule Motion at Surfaces: From Controlled Diffusion to Molecular Motors

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Detailed insight into molecular motion at surfaces is important for understanding various physical and chemical topics as for instance interatomic interactions, molecular growth and self-assembly processes, on-surface reactions and polymerization, atomic-scale friction and the functionality of molecular machines. In this talk, several studies of molecular motion at well-defined single-crystal surfaces, using scanning tunneling microscopy (STM) to characterize molecules moving on surfaces, will be presented.

By reversibly changing the isomeric state of azobenzene tetramers via light-induced switching, their diffusion properties on a surface during STM imaging can be modified [1]. Using the STM tip to manipulate dipolar molecules, these can be either precisely rotated [2] or displaced [3] a surface, also in a pseudo-blind (and therefore much faster) mode without the typical imaging after every manipulation step [4]. In the case of fluorene derivatives, single molecules could be moved with high precision over relatively long distances, even between two independent STM tips (see Fig. 1) [5]. This unique setup, realized in a 4-probe STM, allowed to determine traveling distance and time for a single molecule.

Molecular motors represent an important class of molecules in view of controlled motion [6]. They have been studied intensely in solution, but only little at surfaces. Several studies of molecular motors from our labs will be discussed in this talk where so-called 'Feringa-motors' were manipulated either by heat and light [7] or with the STM tip [8] on metallic surfaces. Moreover, a novel type of motor will be presented, which is based on a simple molecule that does not contain any motor function, but achieves this functionality only in combination with a surface.

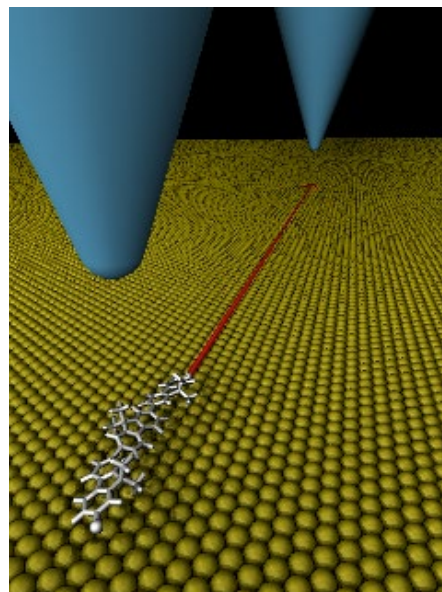


Figure 1: Single-molecule transfer between two STM tips [5].

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Tuning the mechanical properties of single molecules by on-surface reactions

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In this talk, recent scanning tunneling microscopy experiments will be presented, where on-surface reactions are used to tune the mechanical properties of selected molecules, investigating the origin of directed translations and rotations [1].

Azulene based precursors, specifically designed to have a high molecular dipole moment, partially cleave and reassemble forming metal-organic structures with decreasing dipole moments [2]. Furthermore, ring closure reactions of vinylheptafulvene molecular switches can be induced, strongly varying the molecular dipole moment [3]. Both examples allow us to study the role of dipole moment and charge distribution in voltage-pulse manipulation on Au(111).

Thanks to their internal charge separation and the possibility to both chemisorb and physisorb on the Au(111) surface, DMBI-based zwitterionic molecules represent ideal model systems to study directed movements on surface, allowing the comparison of unidirectional rotations and translations in the same experimental conditions [4, 5]. Combining long-time electronic excitations with the slow controlled increasing of the substrate temperature, we investigated the interplay of thermal and electronic excitations for the unidirectional rotation.

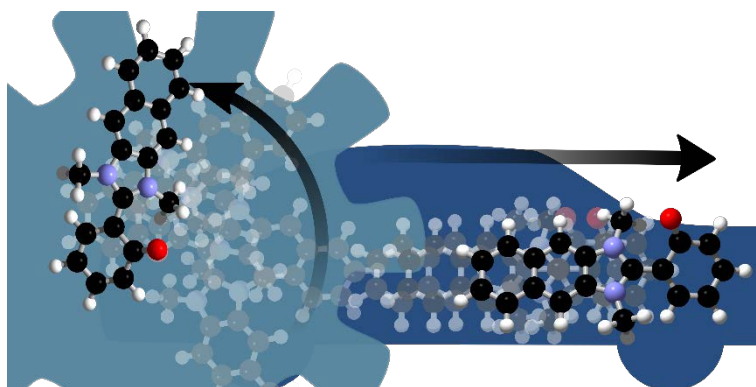


Figure 1. A single-molecule machine showing two distinct functions depending on its adsorption conformation [5].

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Selectivity in single-molecule reactions by tip-induced redox chemistry

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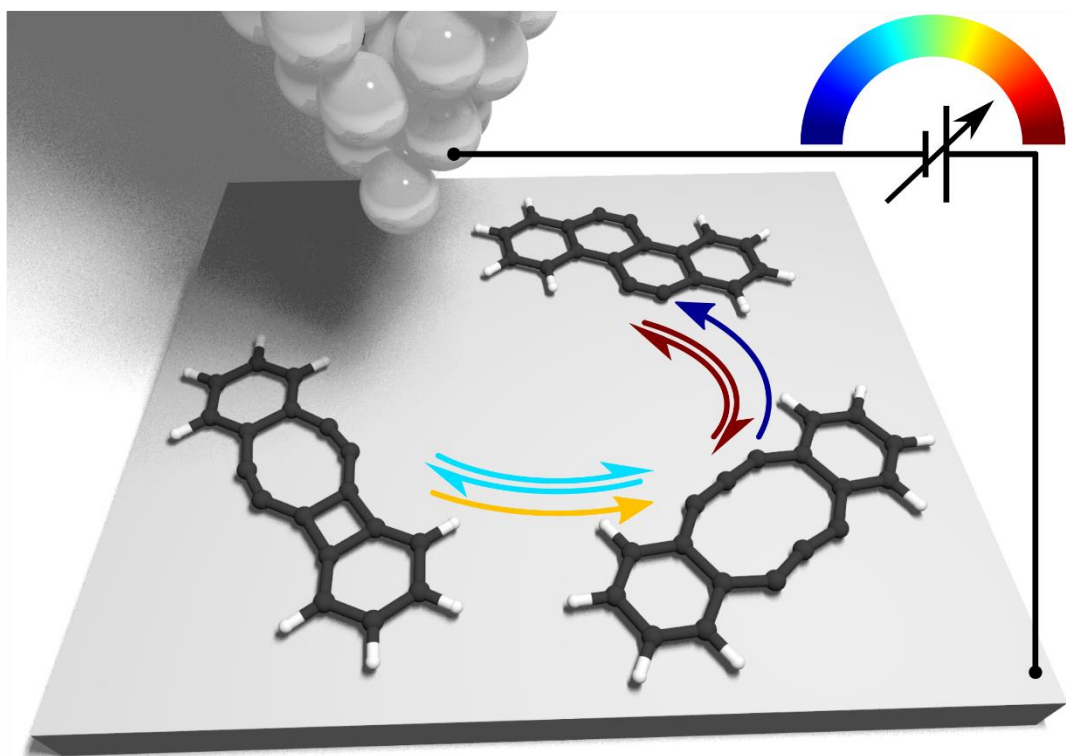
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Since the first experiments by S.-W. Hla in 2000 [1], tip-induced on-surface synthesis is an active field. Not only in on-surface chemistry, selective control over the outcome of a reaction is a major quest. Here, we activate a molecule adsorbed on ultrathin insulating films by dehalogenation and perform selective constitutional isomerization reactions in a low temperature UHV combined STM and AFM. The selectivity is controlled by the polarity and amplitude of applied voltage pulses. The insulating films stabilize the isomers in different charge states and allow for their characterization. The importance of molecular charge state on the reaction is supported by DFT-derived isomerization energy landscape [2].

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Mechanical Properties of Molecular Networks

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Electrons from surface states in Ag(111) become confined in pores of molecular networks, which leads to quantum-dot like behavior as observed by tunneling spectroscopy. Surprisingly, noncontact friction is also affected by these confined states, representing some new kind of energy dissipation mechanism [1].

The assembly of large molecules can be prepared by electrospray deposition and investigated by room temperature and low temperature atomic force microscopy (AFM). A large difference of the lattice constant as a function of temperature is found, which is related to a giant thermal expansion coefficient. The thermal movements of the alkyl chains induce the increase of separations of molecular cores [2]. A dependence of alkyl chain length and substrate will be presented [3].

In addition, a number of solution synthesized graphene nanoribbons (GNR) is deposited on metallic and insulating substrates by electrospray deposition. Twisted nonplanar fjord-edged GNR, methoxy functionalized “cove”-type GNR and longer “cove”-type GNR with alkyl chains are investigated [4]. Depending on the rigidity of the GNRs as well as steric hindrance different structures are observed,

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Bonding and Reactivity on Surfaces: From Fundamentals to Application with Computational Approaches

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Computational approaches based on density functional theory (DFT) are now capable of describing bonding and reactivity for realistic on-surface reactions with good to very good accuracy. We are investigating a wide range of molecule-surface interactions on semiconductor and metal surfaces including organic and inorganic molecules tackling basic research questions up to targeting applications. The talk will cover three parts of this research agenda:

First, I will present work on the reactivity of corroles on Ag(111) where hydrogen-transfer to the surface is driven by regaining aromaticity in the adsorbate molecule.[1]

Second, the surprisingly different surface chemistry of isomers azulene and naphthalene will be presented.[2,3] Aromaticity plays again a key role for their reactivity. More general, non-alternating π -electron systems as a recently discovered class of adsorbates show unusual surface reactivity as shown in more detail in a second contribution from our group.

Third, I want to show the importance of understanding reactivity with and at the surface for area-selective atomic layer deposition.[4,5] This method is a key process for the continuous technological development in the semiconductor industry and the surface chemistry is largely unexplored.

In all research topics, we closely collaborated with groups targeting the research questions from the experimental side.

Additionally, I will showcase the use of our method for analysing surface-adsorbate bonding (energy decomposition analysis for extended systems (pEDA)) for revealing the key electronic factor driving the surface chemistry in many systems.[6,7]

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1D metal-coordinated polymers vs. graphene nanoribbons: influence of chirality and substrate

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Control over graphene's electronic properties is a prerequisite for facilitating the implementation of graphene in future electronic devices. One way to adjust the electronic properties of graphene is spatial confinement of its charge carriers in a 1D structure, so called graphene nanoribbons (GNRs). One recently established route, which also offers flexibility over the structural properties, to create GNRs is on-surface synthesis. [1]

In previous work, we fabricated narrow chevron-like GNRs on Au(111) from the prochiral molecular precursor 6,12-dibromochrysene (DBCh) based on enantiomer-selective Ullmann-type coupling and subsequent thermally induced cyclodehydrogenation (Figure 1a). [2] In addition to the structural characterization of these GNRs by scanning tunneling microscopy (STM) (Figure 1b), we also studied their electronic properties using scanning tunneling spectroscopy, also in dependence of their length and spatial symmetry. [3] Furthermore, we observed different coupling defects resulting in bent GNRs which are based on the formation of both a five- and six-membered carbon ring. This results in the formation of a molecular heterojunction whose electronic properties differ compared to the straight ribbons that constitute it.

To investigate the influence of the substrate onto the GNR formation from DBCh, we employed further coinage metal substrates, namely Ag(110), Ag(111) and Cu(111). For all three substrates, DBCh was found to be dibrominated when deposited onto the substrate held at room temperature. On Ag(110), depending on the annealing treatment, either homo- or heterochiral metal-coordinated 1D polymers were obtained. On Ag(111), different metal-coordinated structures were observed which could be transformed into heterochiral metal-coordinated 1D chains (the most stable and favored arrangement on this substrate) upon annealing. The various intermediate structures provided valuable information on the formation and growth process of these heterochiral chains. Also for Cu(111), the formation of 1D metal-coordinated chains was observed whereas a homochiral arrangement was preferred. [2] Unfortunately, for none of these substrates, the metal-coordinated structures could be transformed into GNRs.

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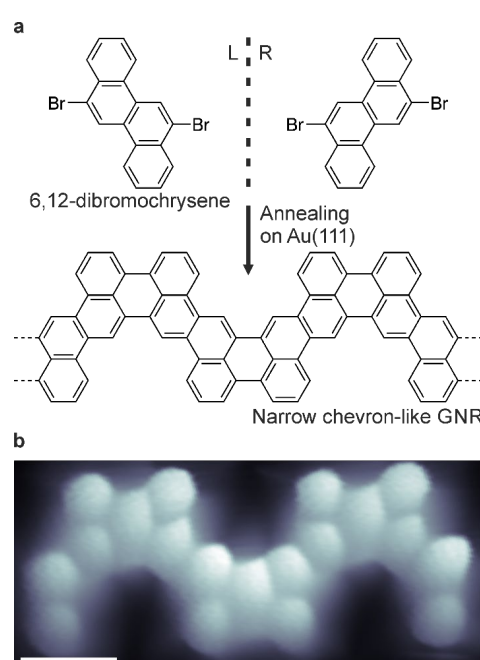


Fig. 1: a) Schematic displaying the two DBCh enantiomers and the chevron-like GNR obtained upon annealing. b) Constant height STM image obtained with a CO-functionalized tip. Scale bar: 5 Å.

PriOSS Symposium
Poster Abstracts

Ullmann coupling reactions on gold nanoparticles

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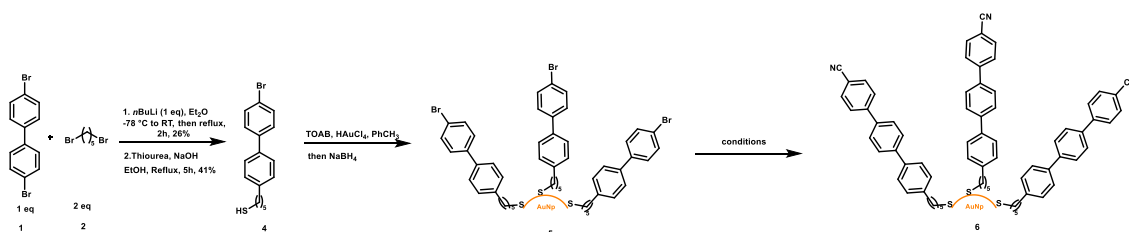
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The Ullmann reaction is one of the oldest coupling reactions. Besides its widespread use, it has been posed with many disadvantages, such as poor functional group tolerance, harsh reaction conditions, as well as poor selectivity towards heterocoupled products.^[1] Most of these aforementioned demerits have been surmounted with appropriate ligands and catalysts, with the exception of clear selectivity between the homocoupled product and the heterocoupled product.^[1] In some cases, the former reaction tends to be faster than the latter, resulting to an appreciable yield of the homocoupled product in Ullmann reactions. Previous work in our collaborative research group has shown that, adsorbing coupling partners to a 2-D Au (111) surface will enable these molecules to be oriented in a manner that they can be dragged and dropped, using a CO-functionalized tip of an Atomic Force Microscope (AFM).^[2] With this technique, organic molecules which hitherto, remained elusive by on-surface synthesis became selectively accessible. Nevertheless, this method is limited to single molecules and not suitable for bulk material synthesis. In a quest to access functionalized hybrid materials in a selective manner, we devised a novel Ullmann reaction on thiol-functionalized gold nanoparticles.

We chose 4,4-dibromobiphenyl **1**, as a model compound due to its similarity with the terphenyl units used in our previous on-surface studies.^[2] A functional group interconversion of **1** gave rise to **4**. Reaction of **4** with HAuCl₄ using the Brust-Schiffrin approach furnished the surface assembled monolayers on the nanoparticles, thereby, setting up the system for an Ullmann reaction with 4-bromobenzonitrile. It is noteworthy to mention that, selectivity towards heterocoupled product was possible due to the orientation of the ligands on the nanoparticles, enabling a proximity for the coupling partner with no proximity for a homocoupled reaction.



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Towards Synthesis of Two-Dimensional Polymers on Metals by Photopolymerization

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A promising way to produce high quality ordered 2D polymers is their synthesis by topochemical photopolymerization. Thereby, the molecules initially self-assemble into a virtually defect-free 2D arrangement driven by weak interactions, such that specific photoactive moieties are in close proximity to each other. Subsequently, covalent C-C bonds between the molecules are created by photochemical excitation. The principle molecular arrangement is hereby largely maintained.

Inspired from successful single-crystal-to-single-crystal and Langmuir-Blodgett approaches [1,2], we were able to produce highly regular 2D polymers on alkane-passivated HOPG with the aid of photopolymerization by using a fluorinated anthracene trypticene (fantrip) molecule (Fig. 1a/b) [3]. As next step, we want to transfer our approach also to metal substrates, since they have various benefits over graphite: (1) well established post-synthetic processes for transfer and (2) macroscopic single crystallinity, which could also aid the on surface synthesis of macroscopically single crystalline 2D polymers.

Herein, we demonstrate our experimental results on Au(111) single crystal surfaces. To obtain a photoreactive self-assembly of fantrip (Fig. 1c/e), passivation of the surface with iodine was necessary [4]. Illumination with violet laser light resulted in a contrast change of the linkages between molecules due to covalent coupling (Fig. 1f/g). The reaction rate on iodinated Au(111) is two orders of magnitude faster than on alkane-passivated HOPG, which might be a consequence of hot electron attachment on the metal. Interestingly, the photopolymerization saturates at ~30% conversion. The underlying photochemical mechanisms are currently under investigation with the aim to attain full polymerization also on Au(111).

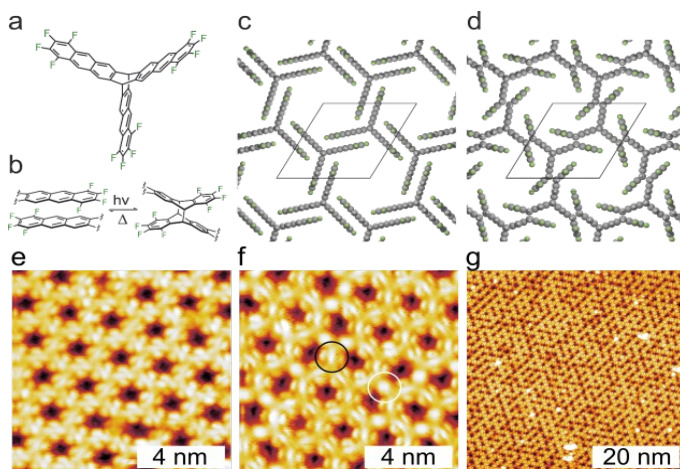


Fig. 1: **a** Molecular structure of fantrip; **b** Illustration of the photoinduced reaction ([4+4]-photocycloaddition) **c** Photoreactive self-assembly of fantrip molecules; **d** Completely cross-linked 2D polymer; **e** STM image of fantrip self-assembly fantrip on iodine passivated Au(111); **f,g** STM images after illumination with violet light; the linkages change their contrast from a butterfly shape (black circle, supramolecular) to a single protrusion (white circle, covalent), which is a result of the covalent coupling; the conversion does not exceed ~30%, also for extended illumination durations.

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Mechanistic Insights into On-Surface Cyclization Reactions

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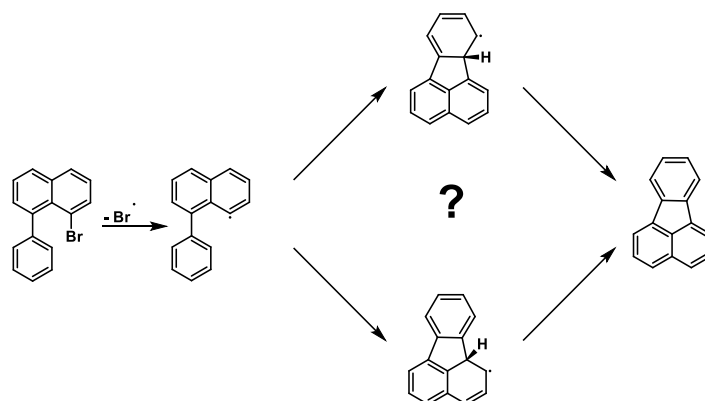
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Organic on-surface reactions are at the interface of organic chemistry and experimental physics. Over the course of the last years it has been shown that various reactions, traditionally performed in-solution, could effectively be performed via an on-surface reaction as well.^[1] Even though having the lack to produce bulk quantities as a bottleneck, it could be shown that a molecule-by-molecule assembly is possible.^[2] This could be key for future applications in the design of polymeric structures of defined dimensions. Among the manifold reactions employed in on-surface reactions, the dehydrogenative C-C coupling as well as the dehalogenative C-C coupling were two of the most prominent ones.^{[3],[4]} While classical in-solution chemistry and its mechanisms are well established and studied in detail, the underlying mechanisms of the more recently evolved on-surface reactions are still rarely investigated and lack an in-depth understanding. In this regard, this crucial understanding needs to be established in order to rationally design reactions as well as target molecules for applications in material research. Especially the complementary to in-solution chemistry makes it a target of interest as complex structures can be designed with a combination of both techniques. In this study, we focused on the investigation of mechanisms towards fluoranthene. Besides the variation of conditions within the on-surface reaction, the design and in-solution synthesis of precursors using traditional organic synthesis methods were key for elucidating the underlying mechanism of the reaction.



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Screening Non-alternant π -Electron Systems for Metal-Organic Interfaces: Interplay between Topology, Aromaticity, and Adsorption Behavior

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Metal-organic interfaces play an important role in organic electronics. Topology, aromaticity, and interface properties are closely connected here as previously shown by experimental and theoretical studies of isomer pairs of alternant and non-alternant adsorbates. While non-alternant 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 by screening a systematic set of molecules using first-principles. However, synthesis of the investigated molecules by conventional approaches is often not straightforward or even not possible and on-surface synthesis could be a promising approach to realize metal-organic interfaces for some of the most interesting molecules.

Here, we report data based on periodic DFT calculations for a set of 11 non-alternant molecules in comparison to analogous alternant molecules. Influence of topology on atomic and electronic structure, especially aromaticity, was analyzed based on molecular gas phase calculations. Interface properties were then derived using slab approaches at the example of Cu(111). We report on the interplay of topology and adsorption structure, adsorption energy, and charge transfer.

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Assigning the absolute configuration of Laurentristich-4-ol

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Assigning the absolute configuration (AC) of molecules is an essential analysis in medicinal chemistry, pharmacology, and natural product synthesis. Two enantiomers of a chiral molecule interact differently with other chiral molecules or chiral electromagnetic fields like polarized light. This results in different chiral properties and functions for the different enantiomers. Since all receptors in the human body are chiral, knowledge of the AC of a chiral drug molecule and the properties of both enantiomers are required before coming to the market. There is no single universal method for determining the AC. The lack of chromophores and small optical rotations are difficulties for the assignment and lead to high uncertainties and misassignments.^[1–3]

In 2018 Schirmeisen, Schreiner, and coworkers demonstrated the use of low-temperature atomic force microscopy (AFM) in assigning the AC of [123]tetramantane.^[4] With a CO-functionalized tip, it was possible to assign the AC by differentiating both enantiomers along their orientation on a Cu(111) surface after visualizing characteristic hydrogen atoms. Different techniques were used in the previous assignment.^[5] First, multiple chiral HPLC separations were required prior to the analytical methods. Single X-ray diffraction required functionalization with bromine and double crystallization. With a $[\alpha]_D$ value of only 34° no interpretable absorptions in the circular dichroism (CD) spectrum were present but a reliable assignment was obtained after matching computed and measured vibrational circular dichroism (VCD) spectra. Recorded optical rotation dichroism (ORD) spectra were also compared with those computed and the structure assigned.

To further demonstrate the power of low-temperature AFM with a functionalized tip, the absolute configuration of (±)-Laurentristich-4-ol should be assigned. After isolation of the naturally occurring (±)-Laurentristich-4-ol from the red alga *Laurencia tristicha* in 2005, the synthesis of the molecule in 2008 revealed the stereochemical misassignment of the structure.^[6,7] Aside from the AC not yet being assigned, several interesting structural motifs, such as the spiro bicyclic motif are present. The reported synthetic plan was followed, however, several steps need to be optimized to obtain a reliable synthesis.

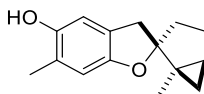


Figure 1 Revised structure of (±)-Laurentristich-4-ol.

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On-surface synthesis and characterization of [19]-starphene

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Starphenes are appealing compounds formed by trimerization of acenes. The potential electronic conjugation of acene arms offers starphenes distinctive physiochemical properties, thus being promising candidates for future organic optoelectronic applications. However, due to the low solubility and instability that large starphenes present, their synthesis has been challenging. To date, the longest starphene obtained by solution-phase synthesis is [16]-starphene [1]. Herein, we propose a new strategy using molecule **1** as precursor to obtain a longer [19]-starphene by on-surface synthesis (Figure 1) on Ag(111). Bond-resolving STM images unambiguously confirmed its chemical structure and the density of states (DOS) of frontier molecular orbitals were resolved by dI/dV maps, further supported by density functional theory (DFT) calculations.

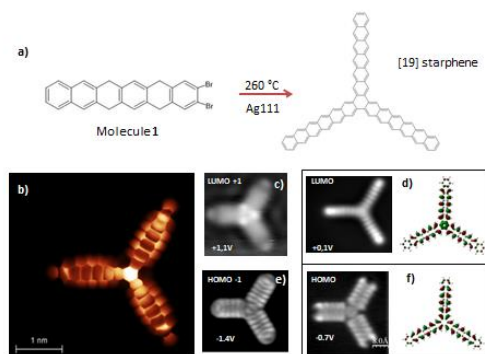


Figure 1. (a) Reaction scheme for the synthesis of [19]-starphene on Ag(111). (b) Bond-resolving STM image of [19]-starphene obtained by using a CO-functionalized probe. (c-f) dI/dV maps showing frontier molecular orbitals of [19]-starphene, together with DFT calculated DOS of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO).

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Adsorption, intermediate formation, and Ullmann coupling of p-terphenyl molecules on Cu(111): influence of the substitution pattern on the final reaction products on the surface

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Dehalogenation of halogenated p-terphenyl molecules and the concomitant formation of metal-organic complexes has been previously studied in detail on the single molecular level [1]. In this contribution, we investigate the influence of the substitution pattern of halogenated p-terphenyl molecules on the final products formed on Cu(111) for different surface temperatures and coverages. In particular, we compare the reaction of 4-bromo-3'-iodo-p-terphenyl with 3-bromo-3''-bromo-p-terphenyl (Fig. 1). Whereas the former molecules form long, irregular chains of metal-organic complexes with limited mobility at 300 K, the final products of the latter ones are dominated by small, regular structures which are highly mobile at room temperature. These regular structures consist of three 3-bromo-3''-bromo-p-terphenyl molecules in cis-configuration connected via a Cu adatom.

Many of these tri-rings prevail after C-C bond formation at elevated surface temperature (700 K) whereas the final products after Ullmann coupling of 4-bromo-3'-iodo-p-terphenyl are dominated by irregular structures with only a small number six-rings arranged in a triangular fashion.

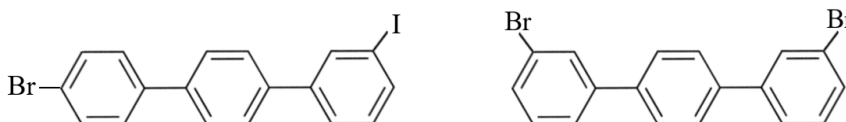


Fig. 1: p-terphenyl molecules investigated in this study.

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On the surface reaction of AzaTrux molecules on Au (111)

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A promising solution for further miniaturization of electronic devices is molecular electronics. Using "bottom-up" techniques, functional organic molecules could be assembled on noble metal surfaces to form elementary nanometer-sized "building blocks" for electronic devices [1]. The goal of this work is to further explore on-surface chemical reactions using specific molecular precursors to synthesize graphene nanostructure. Here we show the bottom-up synthesis of graphene nanostructure on an Au(111) surface using on-surface chemistry (7,12-dibromo-5H-indeno[1,2-a]indolo-[3,2-c]carbazol-15(10H)-one). Structural and electronic properties of graphene nanostructure are characterized by scanning tunneling microscopy (STM) and atomic force microscopy (AFM) with CO-terminated tips.

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Adsorption and mobility of tetracene on coinage metal substrates

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Metal surfaces can act as catalysts to accelerate chemical reactions. In the PriOSS consortium we focus on the Ullmann coupling [1], which profits from the catalytic effect of Cu surfaces. In this contribution, we investigate the adsorption of a model system: Tetracene (four benzene rings) with single Br atom ($C_{18}H_{11}Br$) on coinage metal surfaces from first principles.

In particular, the adsorption of tetracene on the (111) surface of Au, Ag, and Cu is modeled within density functional theory. Total energy calculations reveal the adsorption geometry and energy for the different substrates. For all investigated substrates the molecule is physisorbed on the metal substrate, with van der Waals forces substantially contributing to the binding energy. The latter grows with the atomic number of the substrate. Simulated STM images in the Tersoff-Hamann approximation show the appearance of the molecule for different experimental conditions, both in the constant current and constant height operation mode. The STM-images mainly show p_z orbitals of the benzene rings.

The mobility of the molecule on the substrate is estimated by the calculation of the potential energy surface (PES). The latter is rather flat for Au and Ag substrates, suggesting a high mobility of tetracene. However, the more pronounced PES structures calculated for Cu point out a reduced mobility on Cu substrates.

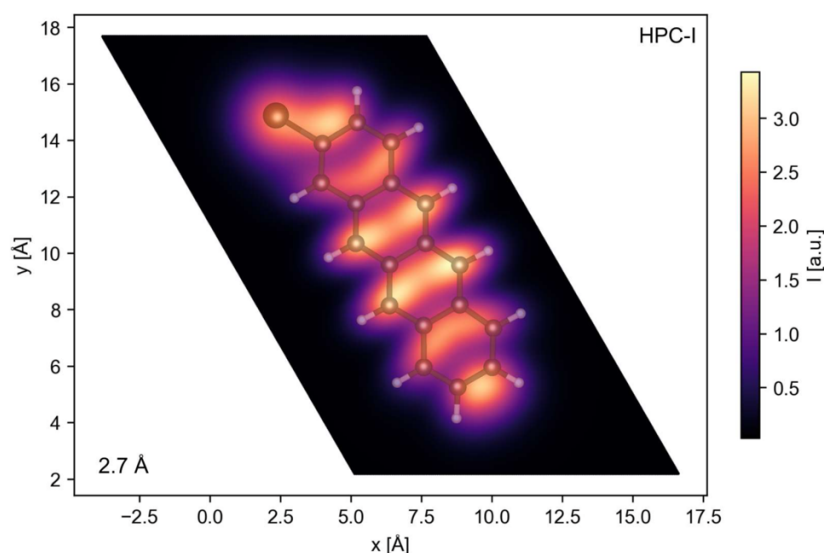


Figure 1: Simulated STM image of tetracene on the Cu(111) substrate in constant height mode (empty states). STM images are simulated within the Tersoff-Hamann approximation and show the p_z orbitals of the benzene rings.

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On-Surface Synthesis of Non-Alternant Nanographenes

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In contrast to benzenoid and alternant structures, molecules with non-alternant binding motifs like azulene show drastic changes in their electronic and optical properties. Acepleiadylene (APD) as a constitutional isomer of pyrene consists of 5-, 6- and 7-membered rings and shows such a non-alternant structure. However, due to its difficult synthesis previously very few studies were conducted. However, a new synthetic route – developed only recently^[1] – makes it possible to pursue surface reactions based on APD. Here we report the successful on-surface synthesis of a non-alternant nanographene based off 1,2-dibromoacepleiadylene (DBA, **1**) on Ag(111), studied by STM, XPS, gas phase DFT and nc-AFM.

Upon annealing **1** on Ag(111), depending on the coverage, high yields of dimer (**2**, **3**) or trimer (**4**, **5**) products can be achieved. At medium coverage (≈ 0.3 - 0.45 monolayers) nearly only dimers were observed. These can further be classified into the trans-dimer (**2**) and the cis-dimer (**3**). At coverages close to a monolayer the formation of the trimer is favored. Depending on the temperature, the organometallic intermediate as well as the covalent nanographene were obtained, as shown by nc-AFM measurements.

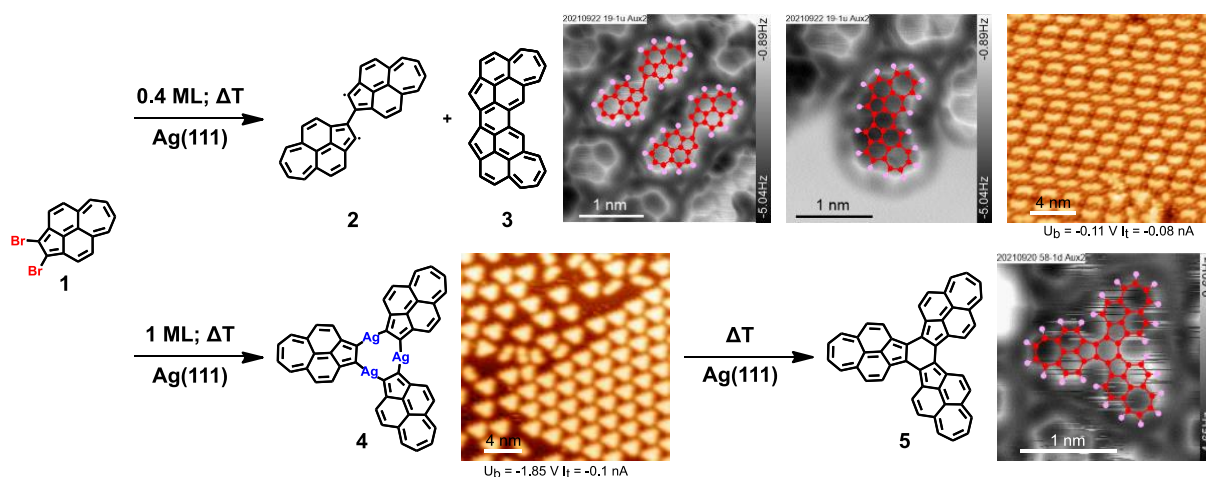


Figure 1: Coverage-dependent reaction of DBA (**1**) to non-alternant nanographenes. Upper pathway: Formation of two acepleiadylene dimers (**2**, **3**) with nc-AFM characterization and large-area VT-STM image. Lower pathway: Formation of extended domains of the acepleiadylene-trimer (**5**) via the organometallic intermediate (**4**), as confirmed by nc-AFM.

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Chemical Bond Imaging of the On-surface Synthesis of Non-Alternant Carbon Nanoarchitectures

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Non-alternant carbon structures contain at least one carbon ring with an odd number of carbon atoms and show different electrical and optical properties compared to their alternant counterparts. An example for a non-alternant structure is Acepleiadylene-dinitrile (APDDN) (Figure 1a) which consists of five-, six-, and seven-membered carbon rings. In this study, we perform the on-surface synthesis of the Phthalocyanine-like molecules 2H-Acepleiadylenocyanine (Figure 1b) and Cu-Acepleiadylenocyanine (Figure 1c) on a Cu(111) surface at a temperature of $T = 510$ K.

These structures could be resolved by constant height atomic force microscopy (AFM) scans with CO functionalized tips at liquid helium temperature ($T = 5$ K). However, due to the non-planar adsorption structure, some parts of the products remain unresolved in conventional constant height AFM scans. As a solution, we show that the chemical bond imaging method with simultaneous tunneling feedback [1] is a powerful tool to reveal the entire structure of non-planar, tightly bound molecules on a metal surface.

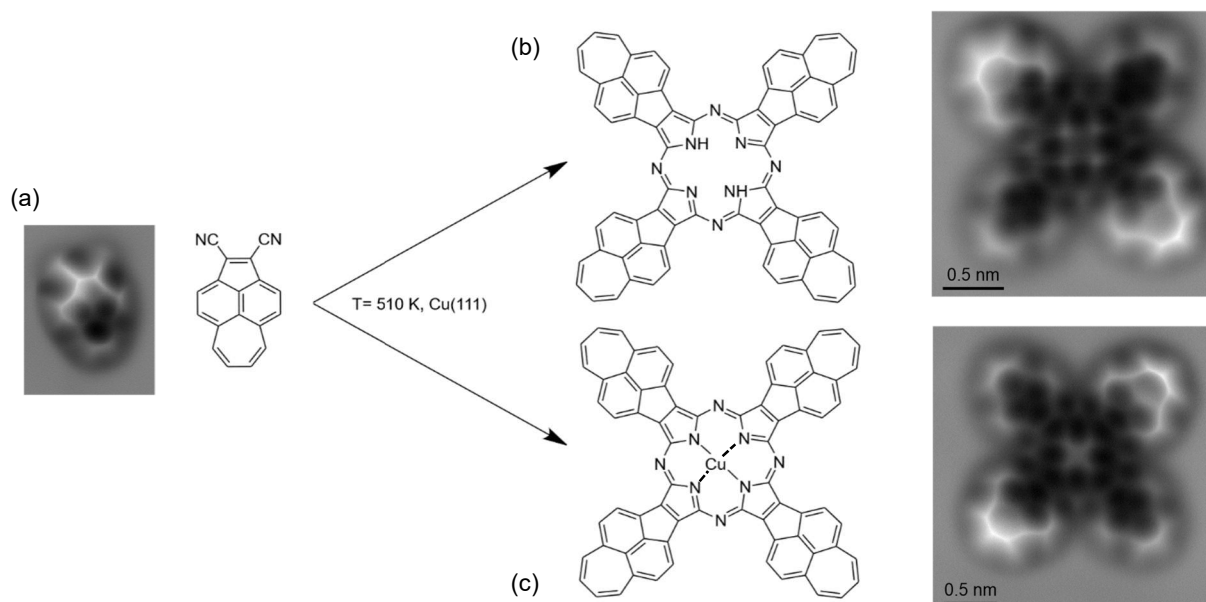


Figure 1: Reaction scheme of (a) Acepleiadylene-dinitrile (APDDN) monomers on a Cu(111) surface at $T = 510$ K. Two different products (b) 2H-Acepleiadylenocyanine and (c) Cu-Acepleiadylenocyanine are formed. The measurements are performed in constant height mode.

Synthesis of Arene-Fused Cyclooctenes and Cyclooctadienes via Bidentate Lewis Acid-Catalyzed Inverse Electron-Demand Diels-Alder Reaction for On-Surface Studies

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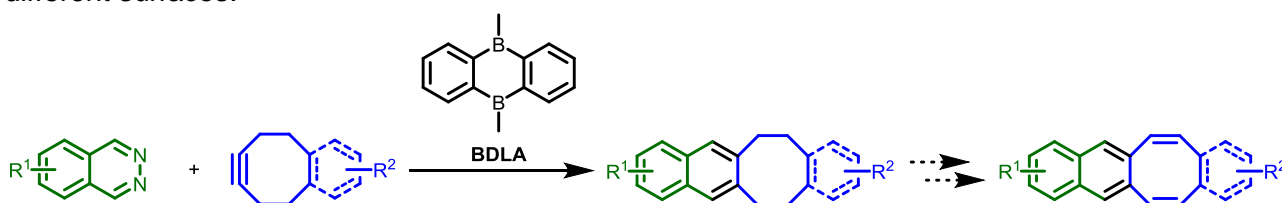
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Arenes fused to eight-membered carbocycles have received significant attention over the past decade in various fields such as photonics,^[1] molecular electronics,^[2] polymer science^[3] and chemical sensing.^[4,5] In particular, molecules consisting of two rigid π -systems linked *via* a flexible cyclooctadiene (COD) or cyclooctatetraene (COT) tether have been shown to exhibit unique, conformation-dependent properties.^[1,6] This led to the use of these structural motifs in fluorescent viscosity probes,^[4] thermally contracting polymers^[3] and molecular tweezers,^[5] among others.

Classically, these COD- and COT-fused arenes are synthesized *via* metal-catalyzed [2+2+2+2] cycloaddition of terminal diynes, photochemical isomerization of bicyclo[2.2.2]octatrienes or Diels-Alder reactions using cycloocta[c]furanes or tetrakis-*exo*-methylene-CODs.^[5,7] While these routes typically lead to symmetric products, CODs/COTs fused to different arenes on both sides have rarely been prepared or investigated.

Herein, we describe a modular approach for the synthesis of arenes fused to eight-membered carbocycles utilizing an inverse electron-demand Diels-Alder (IEDDA) reaction. By using the boron-based bidentate Lewis acid (BDLA) previously established for IEDDA reactions in our group,^[8,9] substituted and unsubstituted phthalazines can be efficiently reacted with cyclooctyne, opening the window for the synthesis of diversely functionalized COD- and COT-fused arenes.

While polycyclic aromatic hydrocarbons (PAHs) consisting of six-membered rings have been studied intensively on surfaces, we envisage to systematically investigate the effect of eight-membered rings on the adsorption and diffusion behaviour by depositing these compounds on different surfaces.



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Building up atomically-precise topological heterostructures in one-dimensional conjugated polymers

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The discovery of topological phases in carbon nanostructures represents a significant development in the field of on-surface synthesis. Recent research has demonstrated that the topological phase transition can be controlled with high precision by adjusting the composition and length of acene-based polymers [1,2], leading to the emergence of topologically protected in-gap end-states.

In this study, we exploit this new design criterion to engineer the quantum phase and locate edge-gap states at specific sites within a single polymer. Using Scanning Tunneling Microscopy and non-contact Atomic Force Microscopy, we investigate the electronic properties and level of hybridization in closely spaced topological states as a function of their separation. The results of this work have implications for the creation of topologically protected quantum spin chains, serving as a blueprint for future research in this area.

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On-surface Synthesis and Characterization of Tridecacene

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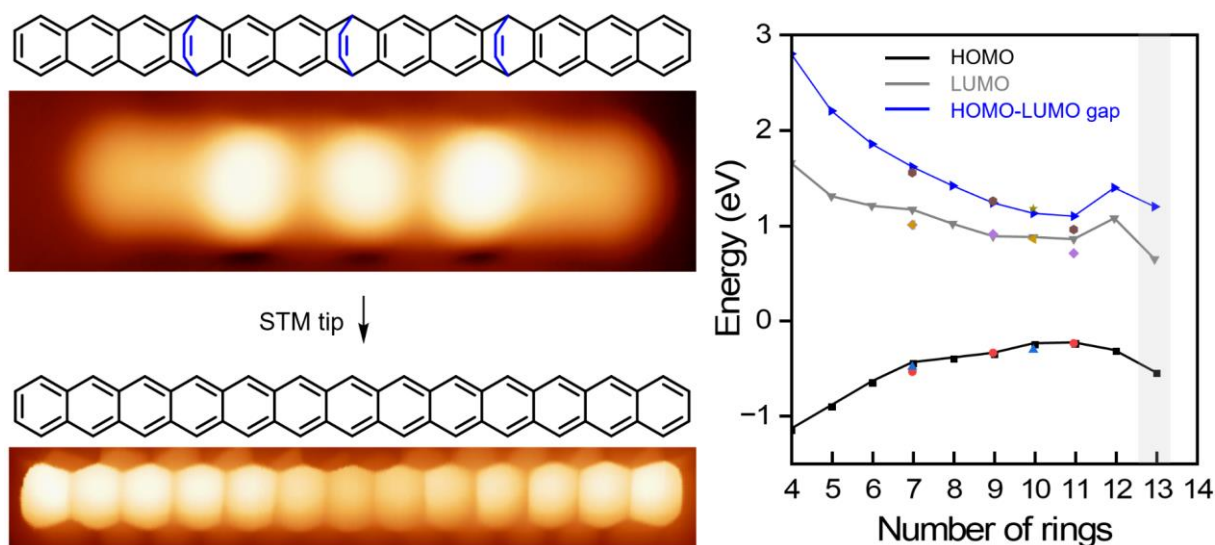
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Acenes represent a unique class of polycyclic aromatic hydrocarbons that have fascinated chemists and physicists due to their exceptional potential for use in organic electronic applications. The comprehensive understanding of their fundamental properties necessitates the expansion of the homologous series towards longer acenes. Here, we demonstrate the on-surface synthesis of tridecacene, 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 investigations, together with first principles calculations. Compared to the shorter acenes, we observed that the HOMO-LUMO gap shrinks again following the gap reopening reported for dodecacene. An antiferromagnetic open-shell ground state electron configuration is found, which is significantly more stable than the closed-shell state. This stability is reduced upon interaction with the Au(111) surface, making the states nearly isoenergetic.

[1] F. Eisenhut, T. Kühne, F. García, S. Fernández, E. Guitián, D. Pérez, G. Trinquier, G. Cuniberti, C. Joachim, D. Peña and F. Moresco, *ACS Nano*, **14**, 1011 (2020)



STM-induced ring closure of vinylheptafulvene molecular dipole switches on Au(111)

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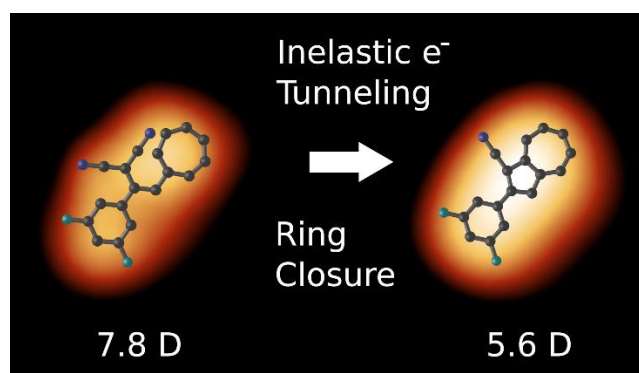
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Dihydroazulene/vinylheptafulvene pairs are known as molecular dipole switches that undergo a ring-opening/-closure reaction by UV irradiation or thermal excitation. Here, we show that the ring-closure reaction of a single vinylheptafulvene adsorbed on the Au(111) surface can be induced by voltage pulses from the tip of a scanning tunneling microscope. This cyclization is accompanied by the elimination of HCN, as confirmed by simulations. When inducing lateral movements by applying voltage pulses with the STM tip, we observe that the response of the single molecules changes with the ring closing reaction. This behaviour is discussed by comparing the dipole moment and the charge distribution of the open and closed forms on the surface.



[1] K. H. Au-Yeung et al., *Nanoscale Adv.*, **4**, 4351-4357 (2022)

On-Surface Synthesis of Kekulene and Isokekulene

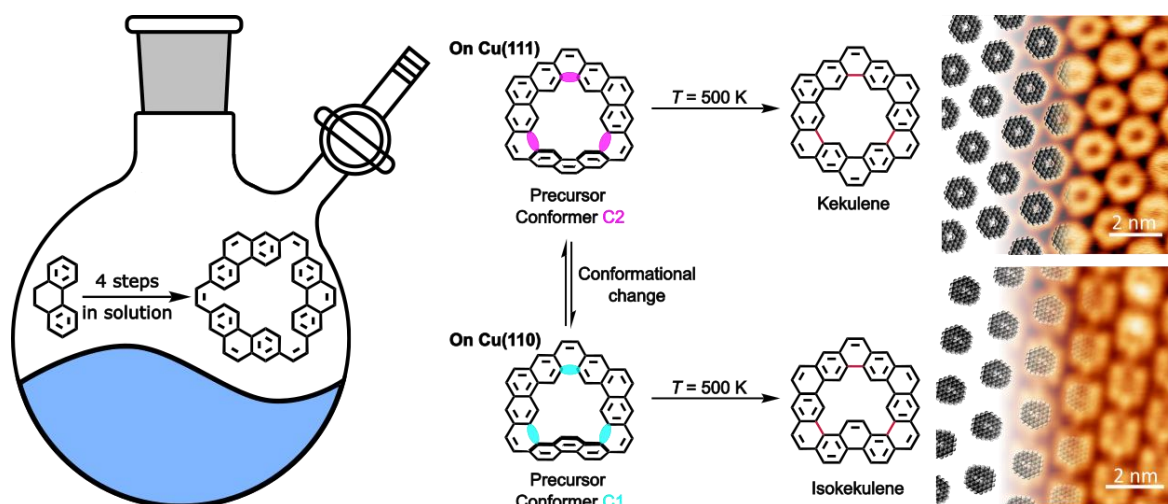
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The concept of aromaticity explains the exceptional stability of monocyclic, planar, conjugated molecules. When extending this concept on cycloarenes, however, the question arises whether the π -electron system is best described by the Clar model or rather by annulenic aromaticity, i.e., delocalization in the inner and outer annulene ring. While vapor deposition of the solution synthesized kekulene is hampered by partial decomposition, it was possible to image single molecules by atomic force microscopy (AFM) and to observe substantial bond localization as predicted by the Clar model [1]. The combination of wet chemistry and on-surface techniques offers the possibility to synthesize complete monolayers of kekulene on Cu(111) from vapor-deposited 1,4,7(2,7)-triphenanthrenacyclononaphane-2,5,8-triene, which undergoes cyclodehydrogenation upon annealing, resulting in extended (up to 100 nm) well-ordered domains of kekulene suitable for investigations by photoemission tomography (PT). Probing the highest occupied molecular orbital with PT supports the description of kekulene's π -conjugation by the Clar model [2]. While the reaction is highly selective towards kekulene on Cu(111) [2], the reaction on Cu(110) leads to an isomer of kekulene with a lower symmetry, named isokekulene. The precursor and the products were analysed with scanning tunneling microscopy (STM), X-ray photoelectron spectroscopy (XPS) and other methods. Further annealing leads to peripheral C–H bond activation and linking towards chains and islands.

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[2] A. Haags *et al.*, *ACS Nano* **14**, 15766 (2020)



Energy transfer-induced fluorescence of a non-fluorescent molecule

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We demonstrate successful activation of fluorescence from nickel phthalocyanine (NiPc) molecules in the junction of a scanning tunneling microscope (STM) by matched resonant energy transfer from other metal phthalocyanines (MPc's) at low temperature. Luminescence of NiPc is usually quenched due to ultrafast intersystem crossing (ISC) and cooling into a dark metal-centered excited state. Our combined STM, scanning tunneling spectroscopy (STS) and STM-induced luminescence (STML) experiments provide evidence that there is an activation barrier for the ISC, which in most experimental conditions is overcome. We show that this is also the case in an electroluminescent tunnel junction where NiPc molecules are adsorbed on an ultrathin NaCl decoupling film on a Ag(111) substrate. However, when placing MPc (M = Zn, Pd, Pt) molecules close to NiPc by means of STM atomic manipulation, resonant energy transfer can excite NiPc without overcoming the ISC activation barrier, leading to Q-band fluorescence. This strategy is applicable to many other cases where luminescence is usually deactivated or quenched.

Theoretical Studies on the Formation of Porous Carbon Nitrogen 2D Networks Derived from of Tricyanobenzene and Tricyanotriazine on Coinage Metal Surfaces

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The field of metal surface chemistry, and in particular on-surface reactions, has attracted considerable attention in recent years. An interesting application that can be investigated using quantum mechanical techniques is the formation of 2D graphene-type organic frameworks for use in nanoscale electronic devices.

Nitrogen-containing “azagraphene” networks are a promising class of systems for such applications. Herein, we present the investigation of the trimerisation mechanisms of highly planar 1,3,5-tricyanobenzene (TCB) and 2,4,6-tricyano-1,3,5-triazine (TCT) on (111) coinage metal surfaces copper, silver, and gold, using density functional theory with dispersion correction. The optimal adsorption positions of both precursors on the three surfaces were determined and their energetic composition was analysed. We show that the molecular mobility on copper surfaces is too limited for proper tri- and polymerisation, especially for compounds with higher nitrogen content, while silver and gold are suitable candidates for these types of on-surface coupling reactions. The interactions between metal and nitrogen were further investigated with respect to their different charge density distributions. Additionally, elucidation of respective polymeric networks created from the selected precursors showed that geometric parameters of silver and gold aid in stabilisation of the finished network whereas the same parameters cause a destabilisation on copper surfaces. These findings may provide guidance for the experimental synthesis of nitrogen-containing graphene networks.

Overall, we present a theoretical view of the on-surface synthesis of nitrogen-containing porous graphene-like networks that can guide experimental synthesis and aid in the selection of a suitable precursor-surface-system.

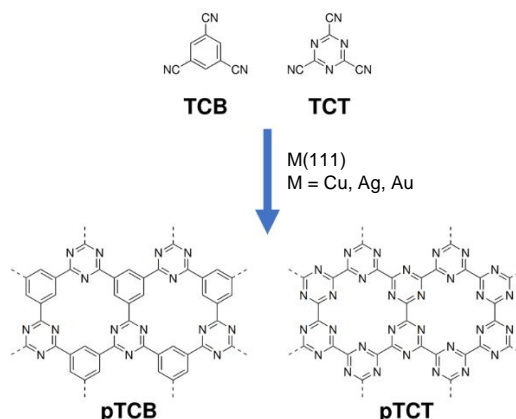


Figure 1: Investigated monomers and polymeric networks

AFM and STM combined study of thiahelicene on Cu(111)

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On-surface synthesis reactions constitute a suitable pathway for the building of functional nanostructures such as nanographenes, nanoribbons and nanowires [1-2]. Among the different available reactions, the Ullman coupling and cyclodehydrogenation have been so far the most used for the study of nanostructured systems. Usually, precursor molecules decorated with halogen groups are chosen, due to the easy halogen cleavage promoted by the catalytic effect of the surface. Studied to a lesser extent is the C-S bond activation [3], which opens the way to new mechanisms for sulfur-containing compounds.

In the present work we addressed the study of the adsorption of thiahelicene molecules on Cu(111). The measurements were carried out in two different experimental system, a low temperature STM (LT-STM) and a room temperature non-contact AFM (RT nc-AFM). Long molecular chains reaching an average value around 200 nm were observed by AFM. During scanning a high mobility of the molecules along the terrace were seen, having an impact in the arrangement and multiplicity of the molecular chains. On the other hands, LT-STM images showed scattered molecules adsorbed on the surface. A gentle annealing can induce the formation of short chains composed by rotated molecules. In addition, further annealing step leads to formation of polymeric chains.

[1] Kawai, S., et al., *Angew. Chem.* **134**,3 (2022).

[2] Zhang, Y., Lu, J., Li, Y., Li, B., Ruan, Z., et al., *Angew. Chem. Int. Edit.* **61**(2022).

[3] Giovanelli, Luca, et al. *Chem. Eur. J.* **28**,47 (2022).

On-Surface Synthesis and Real-Space Visualization of Aromatic P_3N_3

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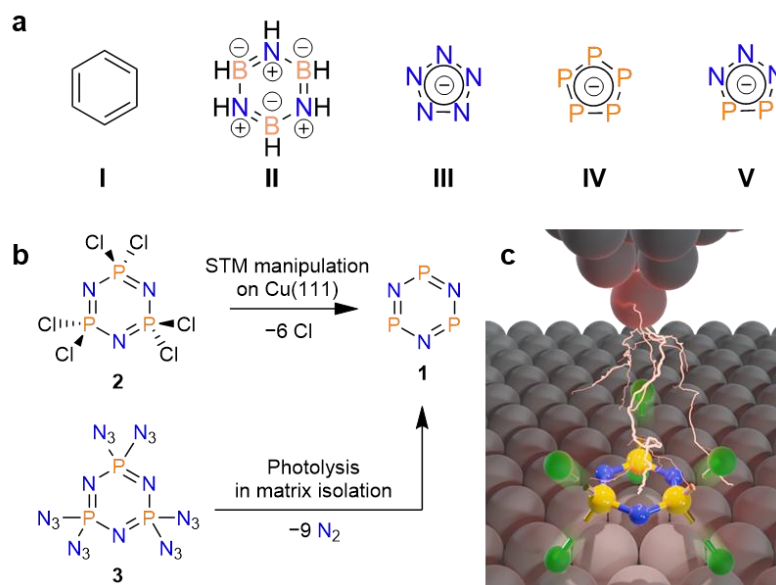
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On-surface synthesis is at the verge of emerging as the method of choice for the generation and visualization of unstable or unconventional molecules, which could not be obtained via traditional synthetic methods. A case in point is the on-surface synthesis of the elusive cyclotriphosphazene (P_3N_3), an inorganic aromatic analogue of benzene. Here, we report the preparation of this fleetingly existing species on a Cu(111) surface at 5.2 K through molecular manipulation with unprecedented precision, i.e., voltage pulse-induced sextuple dechlorination of an ultra-small (about 6 Å) hexachlorophosphazene $P_3N_3Cl_6$ molecule by the tip of a scanning probe microscope. Real-space atomic-level imaging of cyclotriphosphazene reveals its planar D_{3h} -symmetric ring structure. Furthermore, this synthetic strategy has been expanded to generate cyclotriphosphazene via photolysis of a hexaazide (P_3N_{21}) precursor for complementary measurements by matrix isolation infrared and ultraviolet spectroscopy.^[1]



[1] Q. Zhong, A. Mardyukov, E. Solel, D. Ebeling, A. Schirmeisen, P. R. Schreiner, *submitted*, (2023).

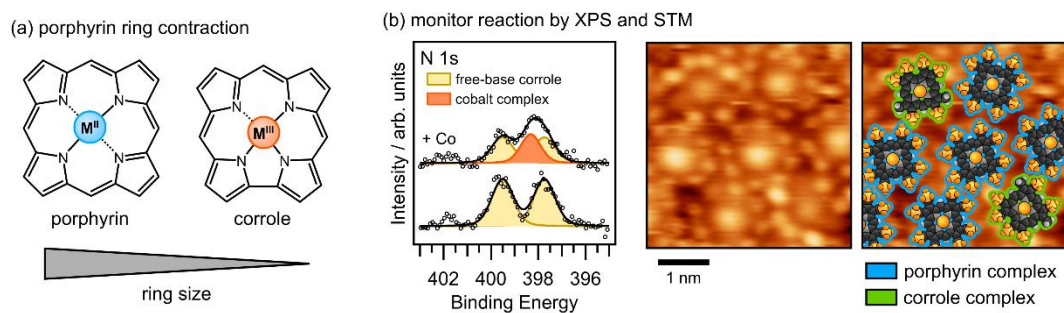
On-Surface Metalation and Demetalation of Tetrapyrroles

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In surface science, tetrapyrrole complexes as porphyrins and phthalocyanines are very popular building blocks for the assembly of two-dimensional molecular architectures in which active metal centers are uniformly distributed.[1] In particular, tetrapyrroles are very attractive because of their versatile complex chemistry and the electronic structure of the incorporated central atom can be easily modified. Thus, the properties of a tetrapyrrole-based interface can be precisely adjusted to a specific application. The surface-mediated metalation of free-base tetrapyrroles by vapor-deposition of transition-metals is an established method for the preparation of tetrapyrrole surface structures.[2]



In our work we have investigated the on-surface metalation of porphyrins and corroles on different coinage metal substrates. The latter represent a smaller macrocycle and provide a tighter coordination environment for the central atom (Fig. a). In addition, corroles act as a trianionic ligand in contrast to the dianionic porphyrin ligands. The choice of the ligand thereby allows to specifically change the electronic state of the central atom. The used surface-mediated metalation of free-base porphyrins and corroles enables access to a wide range of different complexes. We report on the metalation of adsorbed porphyrins and corroles with representative transition metals ($M = \text{Fe}, \text{Co}, \text{Ni}$).[3,4] Furthermore, we have applied the method to the metalation with selected s-Block elements ($M = \text{Li}, \text{Mg}, \text{Ca}, \text{Cs}$) and a heavy post-transition metal ($M = \text{Pb}$). In case of Pb porphyrins we have also observed a thermal-induced transmetalation and demetalation which can be controlled by the choice of the substrate material.[5] The reactions were monitored by XPS and STM (Fig. b).

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[2] H. Marbach, *Acc. Chem. Res.* **48**, 2649 (2015).

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[5] J. Herritsch, S. R. Kachel, Q. Fan, M. Hutter, L. J. Heuplick, F. Münster and J. M. Gottfried, *Nanoscale* **13**, 13241 (2021).