Program Booklet

PriOSS Symposium
Schloss Rauischholzhausen
May 20th – 22nd, 2025

JUSTUS-LIEBIG-UNIVERSITÄT GIESSEN

LOEWE
Exzellente Forschung für Hessens Zukunft

Philipps Universität Marburg

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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.

Daniel Ebeling and André Schirmeisen (local organizers)

PriOSS Symposium 2025 – Program

	Tuesday 20.05.2025	Wednesday 21.05.2025	Thursday 22.05.2025
08:00		Breakfast	
08:30			
09:00		L. Gross	A. Kühnle
09:30		P. Jelinek	R. Tonner-Zech
10:00		H. A. Wegner	M. Gottfried / J. Sundermeyer
10:30		Coffee	Coffee
11:00		L. Chi	M. Lackinger
11:30		A. Schirmeisen	S. Godlewski
12:00		D. Mollenhauer	Closing remarks
12:30	Lunch	Lunch	Lunch
13:00			
13:30			
14:00	M. Corso	S. Kawai	
14:30	S. Clair	J. Björk	
15:00	Coffee	Coffee	
15:30	N. Pascual	X. Feng	
16:00	F. Xiang	R. Pawlak	
16:30	M. Dürr	S. Sanna	
17:00	Poster + Drinks	Poster + Drinks	
17:30			
18:00			
18:30	Dinner	Dinner	
19:00			

PriOSS Symposium - Program

Schloss Rauischholzhausen – 20th-22nd May, 2025

Tuesday, May 20, 2025

12:30-14:00 Lunch

14:00-14:30 Tailoring active sites in graphene nanoribbons for chemical sensing

***Martina Corso**, Centro de Física de Materiales, San Sebastián, Spain*

14:30-15:00 Competing pathways to aromaticity governed by amine dehydrogenation and metal-organic complexation in on-surface synthesis

***Sylvain Clair**, Aix Marseille University, France*

15:00-15:30 Coffee Break

15:30-16:00 Engineering spin configurations in graphene architectures

***Jose Ignacio Pascual**, CIC nanoGUNE, Donostia-San Sebastián, Spain*

16:00-16:30 Open-Shell Porphyrin-Nanographene Hybrid Systems

***Feifei Xiang**, nanotech@surfaces Laboratory, Empa, Dübendorf, Switzerland*

16:30-17:00 Kinetics of the on-surface reactions of p-terphenyls on Cu(111): revealing the rate limiting step towards the final configurations

***Michael Dürr**, Justus Liebig University Giessen, Germany*

17:00-18:30 Poster Session 1

18:30-19:30 Dinner

Wednesday, May 21, 2025

08:00-09:00 Breakfast

09:00-09:30 Chemical reactions and synthesis of cyclocarbons by atom manipulation

***Leo Gross**, IBM Research Europe, Zürich, Switzerland*

09:30-10:00 On-surface UHV synthesis of 2D MOFs and non-benzenoid PAH using π-radical C-C coupling

***Pavel Jelínek**, Czech Academy of Sciences, Prague, Czechia*

10:00-10:30 Expanding the Frontiers of Organic On-Surface Synthesis on Gold Nanoparticles

***Hermann A. Wegner**, Justus Liebig University Giessen, Germany*

10:30-11:00 Coffee Break

11-00:11:30 On-Surface Hydrocarbon Chemistry

***Lifeng Chi**, Soochow University, Suzhou, China*

11:30-12:00 Deciphering the Mechanism of On-Surface Dehydrogenative C-C Coupling Reactions

***André Schirmeisen**, Justus Liebig University Giessen, Germany*

12:00-12:30 Theoretical Insights into On-Surface Reaction Mechanisms and Halogen Bonding on Coinage Metal Surfaces

***Doreen Mollenhauer**, Helmholtz Institute for Polymers in Energy Applications Jena, Germany*

12:30-14:00 Lunch Break

14:00-14:30 On-Surface Syntheses of Three-Dimensional and Heteroatom-Substituted Nanocarbon Materials

***Shigeki Kawai**, National Institute for Materials Science, Tsukuba, Japan*

14:30-15:00 Theory of on-surface reactions: from descriptive to predictive

***Jonas Björk**, Linköping University, Sweden*

15:00-15:30 Coffee Break

15:30-16:00 On-Water Surface Synthesis

***Xinliang Feng**, Technische Universität Dresden, Germany*

16:00-16:30 Proximity-Induced Superconductivity in Molecular Quantum Systems

***Rémy Pawlak**, University of Basel, Switzerland*

16:30-17:00 Computer supported interpretation of imaging spectroscopy: From atomistic simulations to AI based approaches

***Simone Sanna**, Justus Liebig University Giessen, Germany*

17:00-18:30 Poster Session 2

18:30-19:30 Dinner

Thursday, May 22, 2025

08:00-09:00 Breakfast

09:00-09:30 On-Surface Synthesis on the Surface of a Bulk Insulator

***Angelika Kühnle**, Bielefeld University, Germany*

09:30-10:00 Unusual molecules and unusual research questions from first principles: bonding and reactivity on metals

Ralf Tonner-Zech, Universität Leipzig, Germany

10:00-10:30 Combined Solution-Phase and On-Surface Synthesis of Azacoronoids and Long Azaacenes

***J. Michael Gottfried and Jörg Sundermeyer**, Philipps-Universität Marburg, Germany*

10:30-11:00 Coffee Break

11:00-11:30 The Molecular Pressure Cooker

***Markus Lackinger**, Technical University of Munich, Germany*

11:30-12:00 On-surface synthesis on semiconductors and insulators

***Szymon Godlewski**, Jagiellonian University, Krakow, Poland*

12:00-13:30 Closing Remarks and Lunch

Poster Session 1 Tuesday, May 20, 17:00-18:30

P 01 On-surface Synthesis of π-Magnetic Au-Coordinated Porphyrins

***Lenka Cerna**, IMDEA Nanoscience, Madrid, Spain*

P 02 Mechanistic Insights into On-Surface Synthesis by Temperature-Programmed X-ray Photoelectron Spectroscopy

***Lukas Grossmann**, Technical University of Munich, Germany*

P 03 Nonalternant Carbon Nanoribbons with 4–5–6–8 and 5–6–7 Ring Topologies via Polyindenofluorene Fusion

***Dong Han**, Philipps-Universität Marburg, Germany*

P 04 Bottom-up synthesis and characterization of nanoporous graphene structures with graphene or biphenylene-type fusion

***Paula Angulo-Portugal**, Centro de Física de Materiales, San Sebastián, Spain*

P 05 Assigning the absolute configuration of Laurentristich-4-ol

***Kai Feuer**, Justus Liebig University Gießen, Germany*

P 06 Selective On-Surface Synthesis of Isokekulene Facilitated by Strong Molecule-Substrate Interaction

***Sabine Wenzel**, Philipps-Universität Marburg, Germany*

P 07 Tailoring on-surface polymerization by molecular coverage through indenyl coupling

***Alba García Frutos**, IMDEA Nanoscience, Madrid, Spain*

P 08 On-surface Synthesis of Aza-Coronoids

***Tim Naumann**, Philipps-Universität Marburg, Germany*

P 09 Theoretical investigation of 3,3”-dibrom-p-Terphenyl on copper Substrate

***Kevin Eberheim**, Justus Liebig University Gießen, Germany*

P 10 Autonomous manipulations of non-planar molecules in STM

***Nian Wu**, Aalto University, Helsinki, Finland*

P 11 Ullmann coupling reactions on NHC-functionalized gold nanoparticles

***Nathaniel Ukah**, Justus Liebig University Gießen, Germany*

P 12 Spin and charge control of topological end states in chiral graphene nanoribbons

***Kalyan Biswas**, CIC nanoGUNE, Donostia-San Sebastián, Spain*

Poster Session 2 — Wednesday, May 21, 17:00-18:30

P 13 Solution-Based Synthesis of Arene-Annulated Eight-Membered Carbo- and Heterocycles for On-Surface Studies

***Michel Große**, Justus Liebig University Gießen, Germany*

P 14 *Heisenberg S-1/2 antiferromagnetic molecular chain*

***Nan Cao**, Aalto University, Espoo, Finland*

P 15 On-Surface Synthesis and Characterization of Long Azaacenes

***Zilin Ruan**, University of Marburg, Germany*

P 16 Thermally Induced Skeletal Rearrangement of Polycyclic Conjugated Hydrocarbons: A Pathway to Novel Nanostructures

Elena Pérez-Elvira, *IMDEA Nanoscience, Madrid, Spain*

P 17 Surface influences on the molecule identification via fingerprint extraction

Marvin Krenz, *Justus Liebig University Gießen, Germany*

P 18 Quasi-Planar π-Extended Cycloparaphenylenes: Computational Insights into On-Surface Synthesis and Electronic Properties

Jakob Schramm, *Universität Leipzig, Germany*

P 19 On-Surface Synthesis and Reactivity of Biphenylene Network on Au(788)

Ye Liu, Philipps-Universität Marburg, Germany

P 20 *Computational Study of Ullmann Coupling Reaction of Bromobenzene on the Coinage Metal Surfaces*

***Kiyan Linus Haiko Pohl**, Justus Liebig University Gießen, Germany*

P 21 Relating Radical Delocalization, Charge Transfer and Magnetic Ground State in Acene-Derived Oxyradicals

Sergio Salaverría, *Nanomaterials and Nanotechnology Research Center, El Entrego, Spain*

P 22 Precursor synthesis for nitrogen doped graphene nano structures

Olaf A. Kleykamp, Philipps-Universität Marburg, Germany

P 23 On-Surface Synthesis of (1,3)-chGNRs with Five-Membered Ring Edge Extensions

Santiago Galán, *University of Oviedo, Spain*

P 24 *Theoretical Investigation of Dibromopyrene and Iodotriphenylene on Sodium Chloride Coated Copper Substrate*

***Florian Pfeiffer**, Justus Liebig University Gießen, Germany*

P 25 Temperature Induced On-Surface Ring-Opening Polymerization Reaction for the Synthesis of Nanoribbons: Strain Influence of Cycloparaphenylenes

***Miguel Wiche**, Justus Liebig University Gießen, Germany*

PriOSS Symposium

Talk Abstracts

Tailoring active sites in graphene nanoribbons for chemical sensing

Martina Corso[1], Paula Angulo-Portugal[1], Andrea Aguirre[1], Frederik Schiller[1], Manuel Vilas-Varela[2], Jeong Ha Hwang[3], Amogh Kinikar[3], Ignacio Piquero Zulaica[1], Daniel Sánchez-Portal[1], Aran Garcia-Lekue[4], Luca Schio[5], Luca Floreano[5], Roman Fasel[3], Gabriela Borin Barin[3], Diego Peña[2], Dimas Garcia de Oteyza[6]

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A wide variety graphene nanostructures with various functionalities has been created using different on-surface synthesis methods in the past ten years. Among them, graphene nanoribbons (GNRs) showed up as an ideal platform for a wide range of device applications thanks to ability to tune their electronic and magnetic properties with atomic precision.
In this work, we explore the suitability of using functionalized GNRs for gas sensing applications. By surface sensitive techniques in ultra-high vacuum combined with DFT calculations, we demonstrate the capability to tune the electronic structure of semiconducting GNRs by periodic addition at the edges or backbone of functional sites as chemical groups, metal atoms or pores. The addition of cyano (CN) chemical groups dopants at the zig-zag edges of (3,1) chiral GNRs (CN-chGNRs) induces bandgap opening which we associate to a modified conjugation pattern. Efficient coordination of CN groups with metal atoms allows to further tune the electronic structure. In fact, coordination to Fe atoms shrinks the semiconducting ribbons' bandgap to less than half of its value without the metal and shifts the frontiers bands to lower energies. CN groups, similarly to ketone ones [1], protect the ribbons edges and make them stable to controlled O_2 and NO_2 exposure and even in air. Thanks to this enhanced stability, CN-chGNRs survive polymer-free transfer processes to non-conductive substrates [2] proofing the feasibility of their possible implementation in nanodevices.
We finally demonstrate that selective trapping of gas molecules occurs at metallic centers in Fe coordinated CN-chGNRs and in the pores of porous GNRs thus demonstrating an efficient chemical sensitivity of the metal-organic and porous ribbons.
Our work demonstrates that endowing GNRs with functional sites is a robust strategy for the implementation of even reactive GNRs in nanoelectronics and sensing technologies.

[1] J. Lawrence et al., *Nat. Chemistry* **14**, 1451 (2022)

[2] G. B. Barin et al., *ACS App. Nano Mat*. **2**, 2184 (2019)

Competing pathways to aromaticity governed by amine dehydrogenation and metal-organic complexation in on-surface synthesis

Andrés Lombana[1], Songpol Chaunchaiyakul[2], Olivier Chuzel[3], Denis Hagebaum-Reignier[3], Jean-Luc Parrain[3], Franck Bocquet[1], Laurent Nony[1], Christian Loppacher[1], Federica Bondino[4], Elena Magnano[4], Hiroshi Himada[2], Emiko Kazuma[2], Yousoo Kim[2], Luca Giovanelli[1], Sylvain Clair[1]

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We investigated the on-surface reactivity[1] of a *gem*-dichlorovinyl-carbazole precursor on the Au(111) and Cu(111) surfaces by low-temperature scanning tunneling microscopy (LT-STM) and photoemission spectroscopy (XPS), supported by theoretical calculations at the density functional theory (DFT) level. The acceptorless dehydrogenation reaction of the amine moiety was shown to be the decisive parameter governing the selectivity of the homocoupling reaction. A cumulene dimer is formed on the Au(111) surface, which preserves the N-H bond, while a pentalene dimer is formed on the more reactive Cu(111) surface, which induces N-H dehydrogenation. The aromaticity of the respective dimer products is proposed as the driving force leading to the selection of the reaction pathway. This effect is explained in terms of number of pi-electrons injected, depending whether the N lone pair is in-plane (pyridinic-type N) or out-of-plane (pyrrolic-type N), as defined by the hydrogenation state of the carbazole precursor. The presence of the shake-up features in the N 1s XPS spectrum was used as a signature of an extended aromaticity in the pentalene dimer. In addition, we found that the complexation of carbazole with Cu adatom is a kinetically limiting factor, strongly reducing the quality of the polymeric chains formed by high temperature annealing. This kinetic limitation can be overcome by the use of adequate growth conditions.[2]

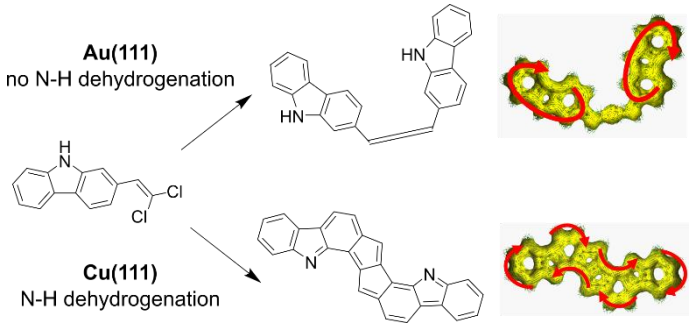

Figure 1: Reaction scheme for the dimerization of the carbazole precursor deposited on the Au(111) and Cu(111) surfaces. ACID calculations (right) show the preservation of the carbazole aromaticity on Au(111), and the formation of a global aromaticity on Cu(111) upon dehydrogenation of the amine.

[1] S. Clair, D.G. De Oteyza, *Chemical Reviews* **119**, 4717-4776 (2019)
[2] A. Lombana *et al*., *Chemical Science* **16**, 3198-3210 (2025)

Engineering spin configurations in graphene architectures

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Graphene nanostructures with custom-designed shapes can exhibit unconventional paramagnetism due to open-shell states in their conjugated π-electron lattice [1]. A key challenge in utilizing nanographene as quantum registers, e.g. collections of qubits, is the localization of highly entangled spins with tunable interactions.

In this work, we present an on-surface synthesis strategy to engineer highly tunable spin states in nanographenes by combining structural design with heteroatom doping. Beginning with an aza-triangulene unit [2], we construct more complex architectures (Fig. 1) [3, 4] that showcase a broad spectrum of spin properties, ranging from high-spin states to topological polyradicalism. The incorporation of a nitrogen heteroatom adds one additional electron to the π-conjugated lattice, disrupting the half-filled scenario predicted by Lieb's theorem [5] and introducing a new parameter for tuning spin states.

We demonstrate that molecular orbital filling plays a critical role in understanding the spin properties of these aza-nanographene platforms. To explore this, we combine low-temperature scanning probe microscopy with quantum chemistry simulations, revealing the nature of the unpaired electrons and their interactions within each nanostructure. Our findings identify promising candidates for a three-qubit register with long coherence times [1], which may be operable via ESR-STM.

We also have worked out strategies to tune spin and charge states by working of substrates of different electronegativity and magnetic configuration, such as GdAu2 and MgO. In this presentation I will also review several results from our group and collaborators that allow us to tune the charge states of the nanographenes and, hence, their spin configuration.

[1] De Oteyza, D. G., Frederiksen, T. (2022) *J. Phys.: Condens. Matter,* 34, 443001
[2] Wang, T. et al (2022) *J. Am. Chem. Soc.* 144, 4522-4529
[3] Vilas-Varela, M., Romero-Lara, F. et al (2023) *Angew. Chem. Int. Ed.* 62, 41, e202307884
[4] Vegliante, A. et al. (2025) *J. Am. Chem. Soc.* In press.
[5] Lieb, E. H. (1989) *Phys. Rev. Lett.* 62, 1201-1204

Open-Shell Porphyrin-Nanographene Hybrid Systems

Feifei Xiang[1], Miguel Martínez García[2,3], Qiang Sun[4], Luis M. Mateo[2], Andres Ortega-Guerrero[1], Nicolo Bassi[1], Roberto Robles[5], Carlo A. Pignedoli[1], Pascal Ruffieux[1], Nicolas Lorente[5], Tomas Torres Cebada[2,3,6], Giovanni Bottari[2,3,6], Roman Fasel[1,7]

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Graphene offers a versatile carbon-based platform for finely controlling physical properties across a broad spectrum. Topologically frustrated nanographenes (NGs) with zigzag edges [1] can translate the sublattice imbalance in their bipartite honeycomb lattice into spin imbalance, as described by Lieb's theorem [2], thereby, giving rise to magnetic ground states [2]. Incorporation of non-hexagonal rings and heteroatoms disrupts graphene's bipartite lattice, resulting in generation of off-zero energy modes and introducing charge carriers, which can significantly alter the magnetic behaviors.

To explore such phenomena, we have developed a new class of open-shell NG systems by incorporating porphyrin units directly into graphene lattice. Porphyrin, with its intrinsic π-conjugated macrocycle, comprising five-membered rings and pyrrolic/iminic nitrogen atoms, not only preserves the π-conjugation in the new hybrid NG structures, but can also enables coordination with transition metal atoms, giving rise to potential spin coupling between π-spins and d/f orbital spins.

In this talk, I will present our recent progress in the synthesis and characterization of open-shell porphyrin-nanographene (Por-NGs) hybrid systems [3,4]. These Por-NG systems exhibit diradical configurations irrespective of their geometric symmetry. The weak hybridization between porphyrin and NG zigzag edge states enables SUMO-LUMO inversion that preserves spin polarization even for the anionic states. Furthermore, the incorporation of magnetic metal centers into the porphyrin cores introduces d–π exchange interactions [5], enriching the magnetic landscape of these hybrid architectures.

1. S. Mishra, et al., Nat. Nanotechnol. **15**, 22 (2020)
2. E.H. Lieb, Phys. Rev. Lett. **62**, 1201–1204 (1989)
3. Q. Sun, et al., J. Am. Chem. Soc. **142**, 18109 (2020)
4. Y. Zhao, et al., J. Am. Chem. Soc. **142**, 18532–18540 (2020)
5. Q. Sun, et al., Adv. Sci. **9**, 2105906 (2022)

Kinetics of the on-surface reactions of p-terphenyls on Cu(111): revealing the rate limiting step towards the final configurations

Mohit Jain[1], Tamam Bohamud[1], Andrii Goriachko[1], Daniel Kohrs[2], Nathaniel Ukah[2], Hermann A. Wegner[2], and Michael Dürr[1]

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In order to experimentally investigate the rate limiting steps of on-surface synthesis reactions, reaction kinetics were followed by means of scanning tunneling microscopy at constant surface temperature. As a model system, halogen-substituted p-terphenyls with different substitution patterns were chosen. On Cu(111), they were previously shown to form metal-organic complexes at room-temperature [1]. For molecules like 3,3"-dibromo-p-terphenyl, two adsorption configurations are possible (Fig. 1); in order to form thermodynamically preferred ring-like structures [2], the molecules which are adsorbed on Cu(111) in the trans configuration have to undergo trans-cis-isomerization.

When we investigated the on-surface reactions of 3,3"-dibromo-p-terphenyl at fixed surface temperature of 300 K, the initially adsorbed molecules linked through C-Cu-C bonds were found in configurations consisting of long, chain-like and only a few shorter, ring-like structures. With the progression of the reaction through time at 300 K, the configurations showed a continuous shift from long chains via more compact structures to ring structures consisting of three molecules. These structures then further aligned to form larger phases of 3-molecule rings. The lateral surface mobility of the molecules was observed to be high at 300 K, however, cleavage and re-formation of the C-Cu-C bond was detected on a much longer timescale; quantitative analysis revealed this C-Cu-C bond cleavage to be the rate limiting step. Trans-to-cis isomerization of the molecules, which is also necessary for closed-ring formation, was observed to be faster and thus not rate limiting. To further consolidate the results, experiments with different substitution patterns of the p-terphenyl molecules were performed.

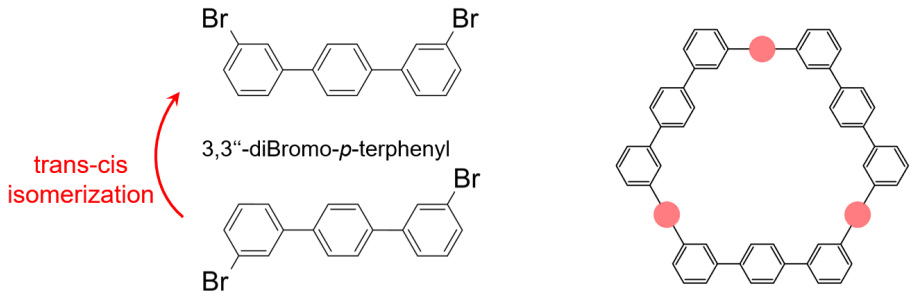

Fig. 1: In order to form thermodynamically stabilized ring-like structures (right, organometallic complex, Cu atoms shown in light pink), 3,3"-dibromo-p-terphenyl molecules adsorbed on Cu(111) in the trans configuration have to undergo trans-cis-isomerization (left).

References:

[1] Ebeling, *et al.*, ACS Nano 13, 324 (2019).
[2] Krug, *et al.*, Chem. Eur. J. **26**, 7647 (2020).

Chemical reactions and synthesis of cyclocarbons by atom manipulation

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Using the tip of a scanning probe microscope, chemical reactions can be induced. To that end, elusive and otherwise unstable molecules can be synthesised on surface and studied with scanning tunnelling microscopy (STM) and non-contact atomic force microscopy (AFM) with bond-resolved contrast [1,2]. The synthesis and characterization of cyclocarbons [3-5], will be presented and control of charge state [6], spin state [7], and selectivity [8] by tip-induced reactions.

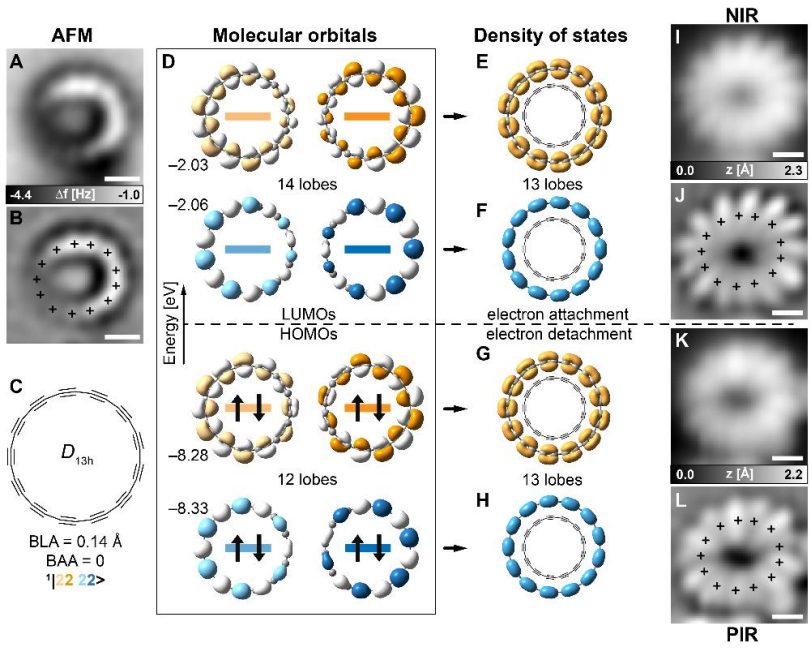

Figure: Cyclo[26]carbon, C_{26}, on monolayer NaCl on Au(111), generated from two C_{13} precursors. (A) AFM and (B) Laplace-filtered AFM data, with the positions of short bonds marked. (C-H) Gas-phase calculations. (I, J) STM at V = 2.0 V, (K, L) STM at V = –2.75 V. (J, L) Laplace-filtered images of (I, K) with the positions of the short bonds (from B) marked. CO tip. Scale bars 5 Å. [5]

References:

[1] L. Gross *et al. Science* **325**, 1110–1114 (2009)

[2] L. Gross *et al. Science* **337**, 1326–1329 (2012)

[3] K. Kaiser *et al. Science* **365**, 1299-1301 (2019)

[4] Y. Gao *et al. Nature* **623**, 977–981 (2023)

[5] F. Albrecht *et al. Science* **384**, 677–682 (2024)

[6] S. Fatayer *et al. Science* **365**, 142–145 (2019)

[7] S. Mishra *et al. Nature Chem.* **16**, 755–761 (2024)

[8] F. Albrecht *et al. Science* **377**, 298–301 (2022)

On-surface UHV synthesis of 2D MOFs and non-benzenoid PAH using π-radical C-C coupling

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In this presentation, I will address two challenges in UHV on-surface synthesis: i) large-scale synthesis of 2D metalorganic frameworks and radical C-C coupling on metal surfaces.

In the first part, I will present a new synthetic approach that enables us to handle two long-standing synthetic challenges in the growth of magnetic 2D MOFs: i) formation of high-quality large-scale 2D MOFs with atomic precision on hundreds of nanometers; ii) design of 2D MOFs with long-range order magnetic coupling with a complex spin texture resulting from the interplay between ferromagnetic and antiferromagnetic π-d interactions. The new synthetic approach consists of forming a high-quality template by supramolecular assembly of the organic ligands [1], followed by the metal coordination by deposition of single atoms, preserving the quality and lattice of the template.

In the second part, we will discuss the possibility of regioselective formation of π-radical, which facilitates inter-molecular radical mediated C-C coupling towards the formation of non-benzenoid polyaromatic hydrocarbons. Resulting non=benzenoid PAH products were characterized by means of a high-resolution SPM technique. The reaction mechanism was rationalized by the free energy QM/MM simulations revealing the importance of Au(111) substrate and single Au adatoms.

[1] F. Frezza et al,, *JACS* **146**, 3531 (2024)

Expanding the Frontiers of Organic On-Surface Synthesis on Gold Nanoparticles

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The advancement of organic on-surface synthesis stands to revolutionize the creation of functional materials, significantly impacting fields such as nanotechnology and device engineering. While traditional research has focused on conducting organic reactions in solution, the emerging potential of surface-level reactions remains underexplored. In this context, we present pioneering research on Ullmann reactions using gold nanoparticles (AuNps) as versatile platforms. By employing thiol-functionalized AuNps, which act simultaneously as reactants, stabilizing agents, catalysts, and reducing agents, we achieve remarkable selectivity in hetero-Ullmann coupling over homo-coupling.[1] This selectivity is driven by the strategic orientation of ligands and the formation of Surface Assembled Monolayers (SAMs). In parallel, we investigate the Ullmann reaction involving aryl halides linked via *N*-heterocyclic carbenes (NHCs) to AuNps in solution, elucidating the vital roles of contact angle, halogen reactivity, and coupling partner proximity on surface reactivity.[2] Our findings delineate crucial parameters for organic on-surface syntheses compared to conventional vacuum-based reactions, with significant implications for materials engineering and molecular self-assembly. This dual approach not only diversifies the toolbox of organic synthesis on surfaces but also opens new horizons for the design of covalent architectures and enhanced device integration.

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On-Surface Hydrocarbon Chemistry

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On-surface chemistry is an emerging interdisciplinary discipline developed in recent years, which presents the great potential in breaking through limitations of traditional chemical synthesis and accurately preparing functional molecular nanostructures. We have made a series of explorations to address the challenging scientific problem of selective C-H bond activation and C-C coupling of saturated alkanes on Au(110) surface [1,2], and further realizing the conversion of alkanes to conjugated polyenes on the surface of Cu(110) as well as interpreting the underline mechanisms[3-8]. More recently, we demonstrated the high selective dehydrogenative aromatization of n-alkane on different metal surfaces[9]. Thereby new methods for the on-surface conversion from n-alkane to conjugated polyene and their aromatization are established.

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Deciphering the Mechanism of On-Surface Dehydrogenative C–C Coupling Reactions

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On-surface synthesis has proven to be a powerful approach for fabricating low-dimensional covalent nanostructures that are challenging for conventional solution chemistry. Dehydrogenative C_{aryl}–C_{aryl} coupling is a popular on-surface reactions, where mechanisms are not well understood due to the lack of microscopic insights into the intermediates that are fleetingly existing. Here, we bypass the most energy-demanding initiation step to generate and capture some of the intermediates at room temperature (RT) via the cyclodehydrobromination of 1-bromo-8-phenylnaphthalene on a Cu(111) surface [1]. Bond-level scanning probe imaging and manipulation in combination with DFT calculations allow for the identification of chemisorbed radicals, cyclized intermediates (Fig.1), and dehydrogenated products. These intermediates correspond to three main reaction steps, namely, debromination, cyclization (radical addition), and H elimination. H elimination is the rate-determining step as evidenced by the predominant cyclized intermediates.

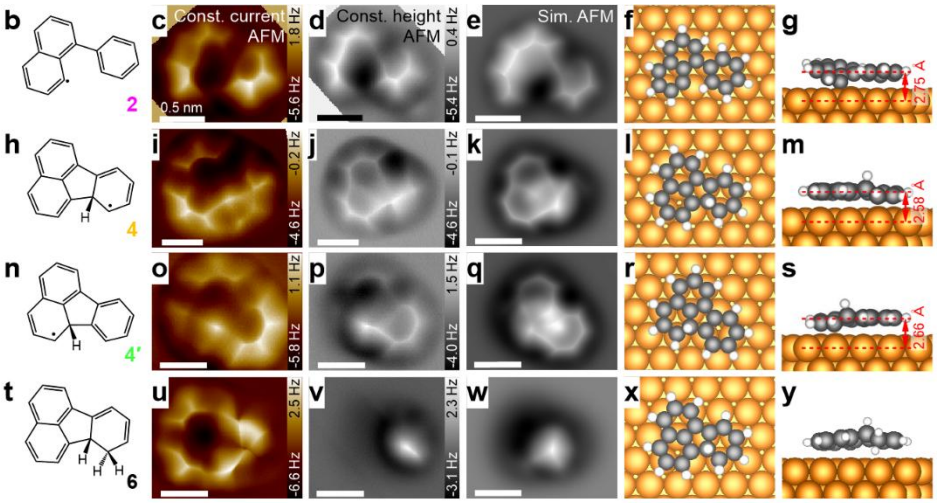

Fig.1. Representative intermediates captured between annealing processes of the BPN/Cu(111)

Furthermore, we have developed strategies to optimize the high-resolution imaging of 3d molecular structures with constant current and adaptive feedback methods [2]. Finally, new results with an active microelectromechanical system (MEMS) microcantilever with integrated piezoelectric sensing are presented.

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Theoretical Insights into On-Surface Reaction Mechanisms and Halogen Bonding on Coinage Metal Surfaces

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Theoretical modeling is of central importance in the understanding of on-surface reactions and molecule-substrate interactions at the atomic scale. Density functional theory (DFT) and semiempirical calculations provide detailed insights into reaction mechanisms and energy landscapes, thus supporting the interpretation of scanning probe microscopy data.

We present a theoretical investigation of the unexpected reversal of halogen bond strengths on Cu(111), where bromine forms stronger interactions than iodine [1,2]. DFT calculations reveal that the σ-hole of iodobenzene tilts significantly upon adsorption on Cu(111), weakening the halogen bond due to reduced orbital overlap. This surface-induced reorientation is much less pronounced on Ag(111) and absent on Au(111), explaining the element- and substrate-specific trends in halogen bonding [1].

Furthermore, the applicability of the semiempirical GFN1-xTB method is evaluated for modeling the adsorption structures of organic molecules on metal surfaces. A structure search algorithm (GMAPF), based on Monte Carlo and molecular dynamics approaches at the semiempirical level of theory, successfully reproduces experimental adsorption sites, demonstrating the method's efficiency for structural screening despite its limited energetic accuracy [3].

Finally, the reaction mechanism of the on-surface cyclodehydrobromination of aryl compounds on Cu(111) is examined in close collaboration with experimental studies. DFT calculations are used to identify the key steps of the reaction pathway—debromination, radical cyclization, and hydrogen elimination—and to characterize the corresponding intermediates observed experimentally. The investigation reveals that hydrogen elimination is the rate-determining step and uncovers an alternative, previously overlooked pathway involving atomic hydrogen-catalyzed hydrogen shifts and eliminations [4].

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On-Surface Syntheses of Three-Dimensional and Heteroatom-Substituted Nanocarbon Materials

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Since the invention of scanning tunnelling microscopy and atomic force microscopy, the manipulation of single atoms and molecules has attracted tremendous interests of researchers. Particularly, combining with bond-resolved scanning probe microscopy,[1] this field has been rapidly developed.

We synthesized three-dimensional organometallic compound and graphene nanoribbon by coupling hexabromo substituted-propellane molecules on Au(111) and Ag(111).[2] In the structure, the C-Br bonds distant from the surface remained intact even after the reaction. The radical species were formed by tip-induced debromination and were also stabilized by either tip-manipulated Br atom or fullerene molecule. We also demonstrate systematic tip-induced isomerization via embedding a text of “NIMS” by following binary and ternary ascii cords, in which two chiral dehydroazulene and diradical units were used (Figure_left).[3] Among the three states, the diradical unit showed the spin coupling of 90 meV within each unit (Figure_middle). However, we found no significant spin exchange coupling between the diradical units, which most probably relates to the large gap of 1.1 nm.

We next synthesized diazahexabenzocoronene on Au(111) and found that the molecule hosts a *S*=1/2 character due to the charge transfer (Figure_right). By covalently linking the molecules on Au(111), we realized spin-1/2 Heisenberg molecular chains with a given antiferromagnetic coupling *J*.[4] These molecular chains show distinct features depending on their parity: gapped excitations for even-numbered spin chains and Kondo excitations for odd-numbered ones.

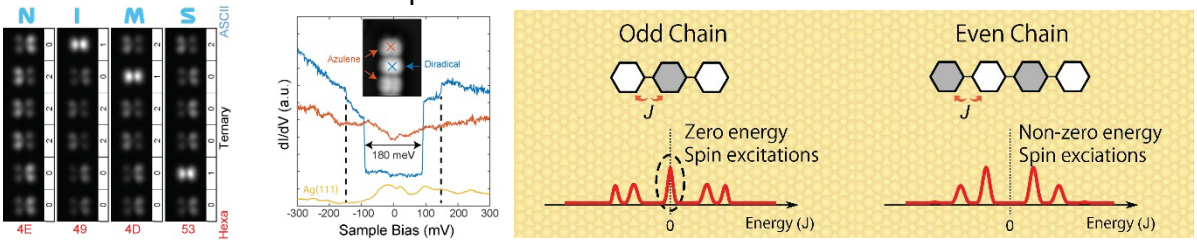

Figure. (left) Systematic local probe isomerization of dehydroazulene units and diradical units on 3D-OMC. “NIMS” in 5-bit ternary ascii code is embedded via sequential isomerization. (middle) d*I*/d*V* curve measured at the diradical unit. (left) Schematic drawing of Heisenberg *S* = 1/2 antiferromagnetic molecular chains composed of odd and even numbers of molecular units and the corresponding magnetic couplings.

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Theory of on-surface reactions: from descriptive to predictive

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On-surface synthesis is a rapidly evolving field, continually revealing new reaction pathways for constructing molecular nanostructures. While experiments can identify reactants, products, and occasionally intermediates, the short-lived transition states that govern reactivity often remain elusive. To enable rational design of surface-assisted reactions, a deeper mechanistic understanding is essential. Here, theoretical modeling – particularly based on density functional theory (DFT) and transition state theory – has become a powerful tool for uncovering the fundamental steps that drive on-surface chemistry.

In this context, we present recent insights that demonstrate both the descriptive and predictive power of theoretical modeling in on-surface synthesis. One example revisits the homo-coupling of terminal alkynes on the Ag(111) surface, a reaction that has been widely studied and discussed over the years. While the butadiyne motif was originally proposed as the dominant coupling product, growing experimental and theoretical evidence supports the enyne linkage as the more prevalent bonding motif. Building on this evolving understanding, our recent theoretical work proposes a new reaction mechanism for enyne formation. Remarkably, it mirrors the previously suggested butadiyne pathway, differing only in the final step [1].

We will also present a new strategy for the on-surface synthesis of triangulene via a thermal route, as an alternative to the commonly used tip-manipulation techniques involving STM or nc-AFM-induced dehydrogenation. While elevated temperatures are often required to overcome activation barriers in on-surface reactions, they can also lead to undesired side reactions and reduced selectivity – an issue that has been particularly challenging in triangulene synthesis. To address this, we propose improving selectivity by lowering activation barriers through the use of single-atom catalysts (SACs). We have systematically screened a range of transition metal atoms doped into both Au(111) and Ag(111) surfaces. Through microkinetic simulations, we identify the most effective SACs for promoting selective triangulene formation. For instance, Ru-doped Au(111) and Ag(111) surfaces are predicted to provide high triangulene yields even near room temperature [2]. Experimental verification of these predictions will be an important step toward validating the proposed catalytic strategy.

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On-Water Surface Synthesis

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On-water surface chemistry occupies a prominent position in scientific disciplines ranging from the origin of life to biological systems, organic transformations, materials science, and environmental science. On-water surface chemistry has been earlier demonstrated for the air-water interface, where it enables the efficient assembly and patterning of molecules, surfactants, macromolecules, and nanoparticles, leading to the formation of ordered structures, including stable monolayers characterized by high surface tension. The unique properties of the water surface provide an intriguing and dynamic environment for chemical transformations, offering distinct advantages over traditional bulk solution chemistry.

Here we will delve into the significance of on-water surface reactivity, selectivity, and the emergence of new reactions, as well as the assembly of molecules and stability achieved on the water surface. By harnessing water-surface confinement and capitalizing on enhanced chemical reactivity and selectivity, on-water surface chemistry provides a powerful synthetic platform. We will particularly present a surfactant-monolayer assisted interfacial synthesis (SMAIS) method that showcases exceptional efficiency in promoting the programmable assembly of precursor monomers on the water surface. Moreover, this method facilitates controlled 1D/2D polymerization, enabling the synthesis of organic 2D crystals with robust functionalities. The organic 2D crystals, including the 2D polymers, 2D conjugated/conducting polymers, and 2D conjugated metal-organic frameworks, generated through on-water surface chemistry exhibit remarkable versatility and hold immense potential across a wide range of applications, including electronics, optoelectronics, van der Waals 2D heterostructures, and membrane devices.

Proximity-Induced Superconductivity in Molecular Quantum Systems

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Low-dimensional magnets proximitized to a superconductor are exciting platform for the realization of a topological superconductor. One of the characteristics of a topological superconductor is the observation of Majorana modes (MM), i.e. zero-energy conductance peaks in the superconducting gap in tunneling spectroscopy or in transport experiments. However, local disorders can severely affect the proximitized superconducting states, which makes the assignment of MM ambiguous. In order to synthesize atomically-precise structures, we propose to use the toolbox of on-surface reactions developed on metallic surfaces (i.e. supramolecular chemistry, coordination chemistry and covalent chemistry [1]) for the synthesis of chains or two-dimensional arrays of spins on superconductors.

In this presentation, we will discuss the challenges in transferring these on-surface chemical reactions to superconducting surfaces [2]. Using low-temperature (1 K) scanning probe microscopy, I will compare the synthesis, structures and spectral signatures by tunneling spectroscopy of coordinated Fe atoms in an iron-based metal-organic chains on Pb(111) and Ag(111) [3]. I then will present our recent works on the supramolecular assembly of radical molecules directly adsorbed on Pb(111), whose charge state can be tuned from anionic to neutral state by the electric field tip of a scanning tunneling microscope (STM) [4-6]. Anionic molecule obtained by an electron donated from the substrate carries a spin-1/2 state, as confirmed by the observation of Yu-Shiba-Rusinov (YSR) states in tunneling spectra at millikelvin temperature. At the border of supramolecular islands, low-energy sub-gap states appear localized at edges with an exponential decay towards the island interior. Tight-binding calculations suggest that their localization lengths and spectral signatures could be consistent with Majorana modes protected by mirror symmetry in an antiferromagnetic spin lattice [6]. In addition, the lateral manipulation of radical molecules on Pb(111) will demonstrated, enabling the construction of complex charge (spin) architectures [5]. Our results open up a vast playground for the synthesis of topological organic-superconductor hybrids.

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Computer supported interpretation of imaging spectroscopy: From atomistic simulations to AI based approaches

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Imaging spectroscopic techniques such as scanning tunneling and atomic force microscopy (STM and AFM, respectively) are of crucial relevance for the investigation of surface-supported structures, including on-surface synthesis processes. These techniques allow to image the investigated system at the microscopic scale, thus enabling a visual interpretation. However, neither STM nor AFM directly reveal the atomic positions. Instead, they map local current and force fields, which must not necessarily correspond to the atomic positions. This makes the interpretation of the collected data non trivial and in peculiar cases even tricky.

Theoretical methods of different accuracy and computational cost are usually applied to interpret experimental imaging techniques and understand the outcome of the measurements. Besides quantum chemical atomistic calculations, which represent the state-of-the-art method to investigate surface supported systems, AI based algorithms are becoming more and more popular [1]. Indeed, machine learning algorithms allow in principle for an automatic structural identification of adsorbed molecules, radicals and intermediate states far beyond the capability of human eyes.

Unfortunately, both quantum chemical methods and AI techniques have limits, as they rely on certain approximations and are not free from pitfalls and uncertainties. In this contribution, we review advantages and disadvantages of modern AFM and STM interpretation tools. Thereby we discuss a few prototypical systems such as halogenated polycyclic hydrocarbon molecules [2] adsorbed on clean or NaCl covered metallic surfaces.

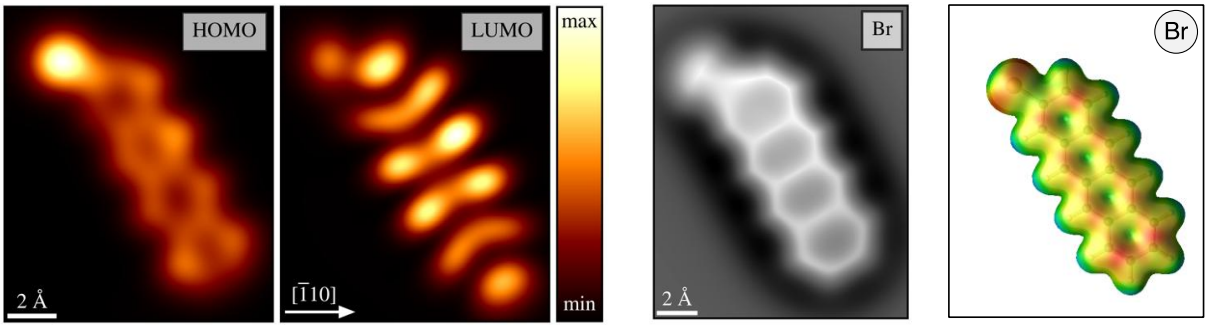

Figure 1: *Simulated STM (lhs HOMO and rhs LUMO), simulated AFM and electrostatic potential images of brominated tetracene adsorbed on the Cu(111) surface.*

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On-Surface Synthesis on the Surface of a Bulk Insulator

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On-surface synthesis has emerged as a fascinating route for creating functional molecular architectures on surfaces that might not be accessible by solution chemistry. An impressive variety of different structures have been achieved by exploiting various synthesis routes, including thermally or as well as photochemically induced reactions. While it has been demonstrated that the substrate can influence the reaction pathway, the majority of all studies presented so far is limited to electrically conducting substrate materials. Here, we present results of on-surface synthesis experiments carried out on the (10.4) cleavage plane of the bulk insulator calcite [1]. On this surface, thermally induced linkage of halide-substituted benzoic acids has been proven possible [2], even in a hierarchical manner [3]. Moreover, photoinduced [2+2] cyclo-addition of C_{60} fullerenes reveals a substrate-templating effect, guiding the reaction in a specific direction [4]. Recently, we benefit from the weak molecule-substrate interaction for photoinduced coupling of fluorinated anthracene triptycene (fantrip) molecules, resulting in a self-assembled structure that favors the topochemical linkage without the need of surface passivation as required for more reactive substrates [5].

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Unusual molecules and unusual research questions from first principles: bonding and reactivity on metals

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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. Our goal is to provide interpretation of advanced experimental measurements and move from there towards prediction of new avenues.

In the first part of the talk, I will present our work on non-alternating π-electron systems. In collaboration with experiment, we moved from the now iconic azulene/naphthalene couple towards larger systems: acepleiadylene/pyrene.[1] Recently, the systematic trends in interface properties for a large range of possible non-alternant molecules promising for on-surface synthesis or deposition were computed and analysed. Several key trends could be revealed.[2]

The second part will cover the theory part of the story towards the longest polyacene. In collaboration with organic synthesis and experimental surface chemistry, we could provide explanations for the unique electronic structure of these intriguing molecules.[3,4]

In the last part, I want to show the importance of understanding reactivity with and at the surface for area-selective atomic layer deposition. This method is a key process for the continuous technological development in the semiconductor industry and the surface chemistry is largely unexplored. Here, the orthogonal reactivity of adsorbates on metal surfaces w.r.t. semiconductor surfaces is key.[5–7]

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Combined Solution-Phase and On-Surface Synthesis of Azacoronoids and Long Azaacenes

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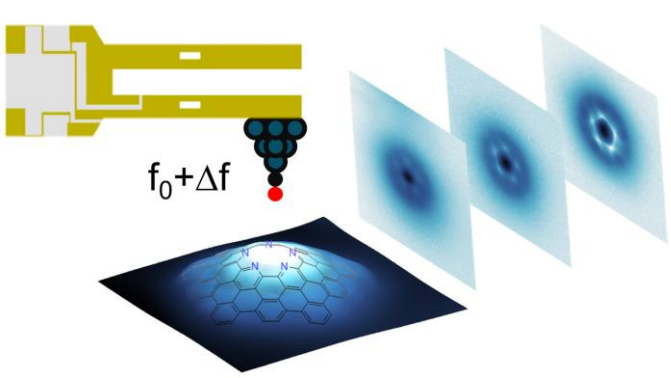
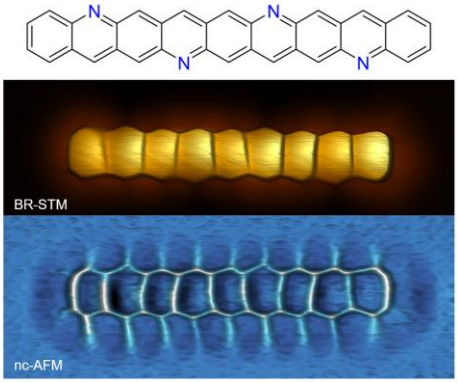
Azaacenes and azacoronoids represent two distinct classes of nitrogen-doped nanographenes with tailored electronic and magnetic properties. By introducing electronegative nitrogen atoms into the acene backbone or within coronoid cavities, the energy alignment of frontier orbitals can be tuned and stability against oxidation enhanced. We report the on-surface synthesis of two long azaacenes, tetraazanonacene and hexaazatridecacene, via atom-manipulation-induced dissociation of a triethenо-bridged precursor on Au(111) under ultra-high vacuum. Additionally, a series of azacoronoids were obtained by combining in-solution and on-surface techniques. The coronoid precursors are based on the same basic framework and possess a dibrominated pyridyl-functionality. By modification of their substituents, edge termination and conformation of the formed coronoids can be controlled. Besides planar armchair- and zigzag-edged structures, a nonplanar, curved azacoronoid and various metal-coordinated azacoronoid complexes were synthesized. The resulting nanostructures were characterized using low-temperature scanning tunneling microscopy/spectroscopy (STM/STS) and non-contact atomic force microscopy (nc-AFM). For tetraazanonacene, an increased frontier orbital gap was observed compared to pristine nonacene, while hexaazatridecacene exhibits an open-shell singlet ground state with a singlet–triplet gap of 110 meV. This joint study highlights the potential of combining complementary synthetic strategies to expand the diversity of nitrogen-doped carbon nanostructures and to uncover structure–property relationships in extended π-conjugated systems.





The Molecular Pressure Cooker

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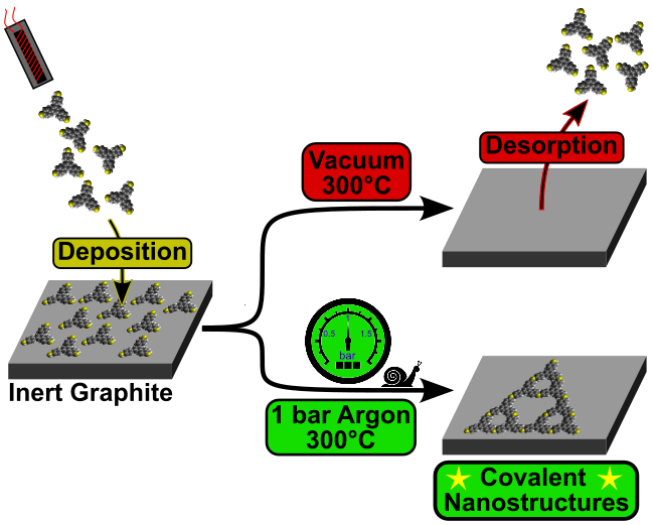
Synthesis on inert and insulating surfaces presents a formidable but rewarding challenge.[1] Thermal coupling is severely hampered by premature desorption of the reactants from these weakly interacting surfaces during annealing. In contrast, the commonly used coinage metal surfaces facilitate a wide range of coupling reactions through the combined effect of increasing the desorption energies of the reactants and lowering the activation energies for coupling. Both effects together ensure that the molecules remain adsorbed throughout the reaction. Although widely used, metal surfaces are associated with serious drawbacks: **(1)** Notwithstanding the fact that metal surfaces are unsuitable for electronic applications and inevitably require transfer, strong adsorption distorts the intrinsic electronic and structural properties of the molecular material. **(2)** Metal surfaces also promote decomposition, limiting the thermal stability of the nanostructures. **(3)** Finally, metal surfaces themselves are prone to contamination and oxidation, making them unsuitable for transferring samples to ambient conditions.

As a novel approach to thermal coupling on inert surfaces, we propose to perform the annealing step in a noble gas atmosphere instead of in a vacuum. Using 1,3,5-tris(4-mercaptophenyl)benzene (TMB), we demonstrate that annealing in ~1.0 bar argon kinetically inhibits desorption up to the extent that thermal coupling of the TMB molecules *via* carbon-sulfur-carbon thioether bonds becomes feasible on inert graphite and even more weakly interacting graphene surfaces.[2] The resulting covalent thioether Sierpinski triangles on graphite are much more thermally robust than their counterparts on Au(111) and are also air stable. We anticipate that other well-established coupling reactions of On-Surface Synthesis can be transferred from their ancestral metal to inert surfaces using this new protocol.



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On-surface synthesis on semiconductors and insulators

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In recent years the on-surface manipulation and chemical reactions created a playground for atomically precise synthesis and development of new atomic and molecular nanostructures. While the surface assisted synthesis approach has proven its effectiveness in the precise formation of new organic compounds on metallic surfaces one of the most challenging limitations arises from the deep dependence on the catalytic activity of the substrate. This makes the direct transfer to the technologically desired non-metallic surfaces extremely challenging. Therefore striving for the generation of desired systems forces the search of new reaction pathways and catalytic transformations.

In this talk I will discuss our attempts for the synthesis of molecular nanostructures directly on semiconductors and insulators. This will be exemplified by the polymerization on two faces of rutile titanium dioxide [1-3], as well as by planarization reactions including cyclodehydrogenation [3] and cyclodehydrofluorization [4] on selected faces of rutile titania. Further, I will present the unprecedented dimerization leading to the pioneering synthesis of well-shaped heteroatom doped nanographenoids on a semiconducting surface. Finally I will demonstrate our approach based on the application of hydrogen atoms as catalysts in the planarization reaction yielding well-shaped nanographenes on different substrates ranging from metals, through semiconductors, up to bulk insulators [5]. The new method provides prospects for circumventing the need to exploit the catalytic role of metallic substrates.

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PriOSS Symposium

Poster Abstracts

On-surface Synthesis of π-Magnetic Au-Coordinated Porphyrins

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Π-magnetic compounds on surfaces have emerged as a powerful platform to interrogate spin interactions at the atomic scale, with great potential in spintronics and quantum technologies. [1] A key challenge is organizing these compounds over large length scales while elucidating their resulting magnetic properties, being coordination chemistry ideally suited for this purpose. Herein, we present the on-surface synthesis of low-dimensional coordination polymers based on open-shell porphyrins using a porphyrin precursor equipped with trans-carbonitrile moieties. Scanning probe microscopy studies combined with theoretical calculations reveal that deposition on hot Au(111)/mica substrate leads to the formation of distinct coordination architectures, including non-magnetic Au-CN coordinated monomers, covalent porphyrin dimers, and one-dimensional porphyrin polymers. Upon tip-induced dehydrogenation, closed-shell species are converted into open-shell, featuring a S=0 ground state displaying localized magnetic moments without observable magnetic exchange coupling between adjacent units [2, 3]. Our study highlights the synergy of on-surface covalent synthesis and coordination chemistry in assembling periodic arrays of π-electron magnetic porphyrins while preserving their spin states, offering new avenues for quantum materials and molecular spintronics. [4]

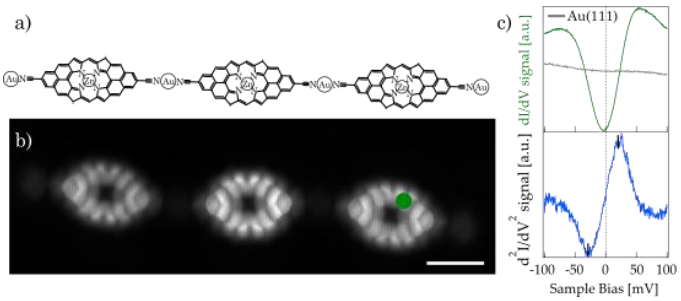

Figure 1. A three-membered porphyrin chain based on tip-induced open-shell monomers. a) Chemical scheme of the oligomer. b) STM image of the porphyrin oligomer at constant height. Scanning parameters: 20 mV. Scale bar = 1 nm. c) dI/dV and d^2I/dV^2 spectroscopy on a monomer within the polymer at the position indicated by the green dot in b).

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Mechanistic Insights into On-Surface Synthesis by Temperature-Programmed X-ray Photoelectron Spectroscopy

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On-surface reactions are often governed by kinetics rather than thermodynamics. Irreversibility is caused either by large exothermic reaction enthalpies or by the loss of volatile by-products.[1] In this respect, temperature-programmed X-ray photoelectron spectroscopy (TPXPS) has evolved to a useful analytical tool for studying reaction kinetics with a sufficient time resolution and excellent statistics.

Two related molecules are studied on Ag(111), 3BPT and 2BPT (Fig. 1a). Both molecules share an identical scaffold, yet differ in the number of brominated sites. Progressive heating drives the two well-known reaction steps of Ullmann-type couplings: **(1)** debromination which results in the organometallic intermediate where molecules are linked via C-Ag-C bonds; **(2)** transition into covalently C-C bonded nanostructures (Fig. 1b). According to their bromine substitution, 3BPT reacts into 2D networks[2], while 2BPT forms rings and zig-zag chains.

Both molecules exhibit similar debromination kinetics (Fig. 1c). Here, the use of isothermal segments instead of a linear temperature ramp allowed us to deduce both the pre-exponential and activation energy, suggesting a second order rate law.[3] By contrast, pronounced differences were found for the covalent transition, which is unambiguously shifted to higher temperatures for 3BPT (Fig 1d).

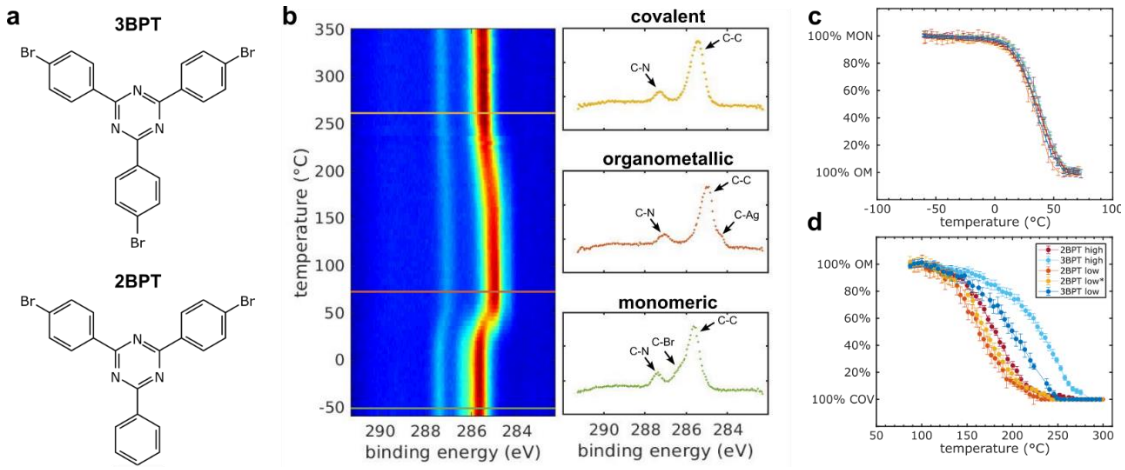

Figure 1: **a** Chemical structures of 3BPT and 2BPT. **b** Exemplary TPXPS data of the C 1s core level of 3BPT on Ag(111). Representative XP spectra of the three stages are depicted on the right. **c** The debromination over temperature was similar for 2BPT and 3BPT and showed no influence of coverage (all measurements plotted, MON = monomeric, OM = organometallic). **d** The covalent transition over temperature revealed a significantly increased reaction temperature for 3BPT, which further increased for higher coverages (low = low coverage (~30% of a full monolayer); high = high coverage (~50% of a full monolayer), OM = organometallic, COV = covalent).

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Nonalternant Carbon Nanoribbons with 4–5–6–8 and 5–6–7 Ring Topologies via Polyindenofluorene Fusion

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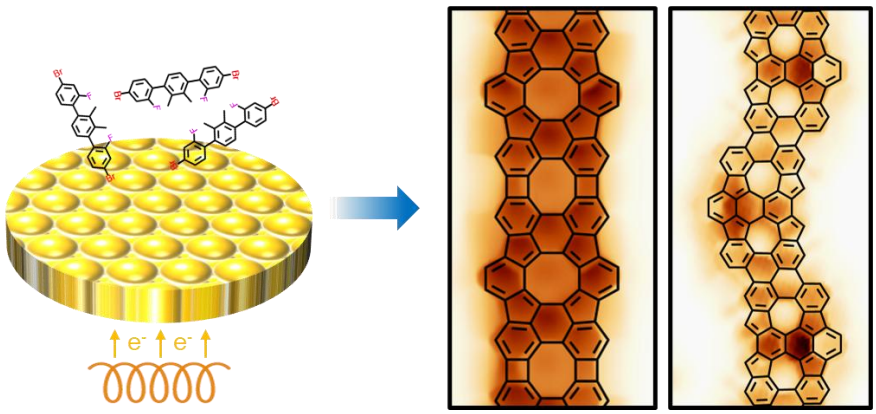
Carbon nanoribbons (CNRs) incorporating nonhexagonal rings [1] represent a compelling class of low-dimensional carbon materials with tunable electronic and magnetic properties that go beyond those of conventional graphene nanoribbons (GNRs) [2]. Here, we report the on-surface synthesis and detailed characterization of two unprecedented nonalternant CNRs composed of a variety of polygonal units: a linear 4–5–6–8 nanoribbon and a zigzag 5–6–7 nanoribbon. These CNRs are obtained via the lateral fusion of cis- and trans-linked indeno[2,1-a]fluorene (IF) polymer chains, formed through sequential debrominative and dehydrogenative C–C coupling reactions of a designed aryl halide precursor. Bond-resolved scanning tunneling microscopy (STM) and non-contact atomic force microscopy (nc-AFM) unambiguously confirm the atomic structure of the nanoribbons, while scanning tunneling spectroscopy (STS) and density functional theory (DFT) calculations reveal their distinct electronic properties arising from the presence of nonhexagonal rings. X-ray photoelectron spectroscopy (XPS) further elucidates the reaction pathway and identifies intermediate species. This study demonstrates a controlled on-surface synthetic route to architecturally complex nonhexagonal CNRs and provides valuable insights into their structure–property relationships, paving the way for novel carbon-based quantum materials.



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Bottom-up synthesis and characterization of nanoporous graphene structures with graphene or biphenylene-type fusion

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Modification of the electronic properties of graphene is crucial for its implementation in semiconductor devices, as field-effect transistors. Band gap tuning of semi metallic graphene can be achieved by various methods, such as reducing its dimensionality, by doping with heteroatom or by introduction of defects as nanopores. On-surface synthesis (OSS) allows for the synthesis in ultra-high vacuum of modified graphene nanostructures with atomic precision as nanoporous graphene (NPG) [1]. In this work, we explore the OSS of periodic porous graphene nanoribbons (p-GNRs) and NPG structures on Au(111) and Au(788) surfaces starting from 7,10-dibromo-1,4-diphenyl-triphenylene molecular precursors [2,3]. Scanning tunneling microscopy (STM) and angle-resolved photoemission spectroscopy measurements show that p-GNRs exhibit semiconducting behavior with a low density of defects. Additionally, thermal annealing of high-coverage p-GNRs at 500°C triggers the lateral fusion of p-GNRs leading to the formation of two families of NPG structures: one with a graphene-like fusion pattern and another one with biphenylene-like lateral fusion (see figure 1). The structural properties of these NPGs were characterized by low temperature STM and non-contact atomic force microscopy (NC-AFM). Density functional theory calculations show that the electronic properties are mainly determined by the carbon backbone between the pore segments, thus they are semiconductors with a smaller band gap than the precursor p-GNRs. Interestingly, while graphene-like NPGs have a direct bandgap, the insertion of biphenylene moieties causes further gap reduction and a change to indirect bandgap. Finally, the exposure to O_2 and CO was explored. We find the pores to be preferential adsorption sites for CO.

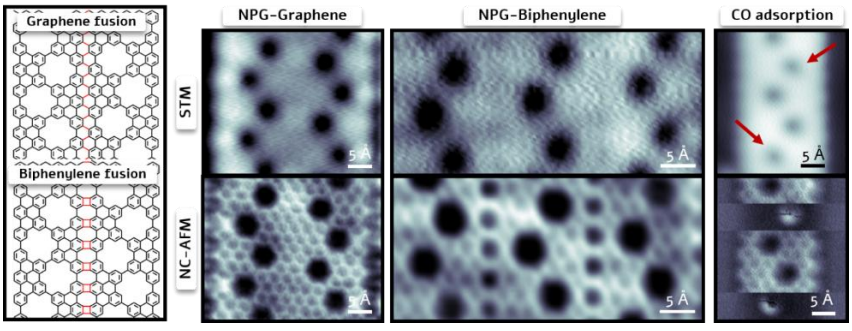

Figure 1. Scheme, LT-STM and NC-AFM images of graphene-type and biphenylene-type NPG structures. Arrows point to the pores where CO molecules are adsorbed.

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Assigning the absolute configuration of Laurentristich-4-ol

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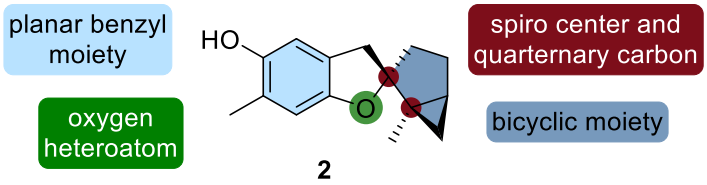
Assigning the absolute configuration (AC) of molecules is an essential analysis in medicinal chemistry, pharmacology, and natural product synthesis. Since two enantiomers of a chiral molecule interact differently with other chiral molecules (e.g. receptors in the human body) or chiral electromagnetic fields (e.g. polarized light), different chiral properties or functions result for the different enantiomers. Especially for chiral drug molecules, knowledge of the AC and the properties of both enantiomers are important and required before coming to the market. Different techniques to assign the AC are available, however no single universal method is available. For molecules without chromophores and those with small optical rotation values the assignment is difficult and has led to high uncertainties and misassignments.[1-3]

In 2018, Schirmeisen, Schreiner, and coworkers demonstrated the assignment of [123]tetramantane **1** with the use of low-temperature atomic force microscopy (AFM).[4] With a CO-functionalized tip, characteristic hydrogen atoms of the different enantiomers of **1** were visualized and thus their characterization was possible. In comparison to the visual inspection by AFM, the previous assignment of **1** included the use of several techniques, starting with multiple HPLC separations prior to analytical methods.[5] For single X-ray diffraction, functionalization with bromine and double recrystallization was necessary. Due to the low $[\alpha]_D$ value of 34°, no interpretable absorptions in the circular dichroism (CD) were present. A reliable assignment was only obtained after matching computed and measured vibrational circular dichroism (VCD) spectra and optical rotation dichroism (ORD) spectra.

To further demonstrate the power of low-temperature AFM, the AC of (±)-Laurentristich-4-ol **2** should be assigned. The synthesis of **2** in 2008 revealed the previous stereochemical misassignment of the structure after its isolation in 2005.[6,7] Aside from the AC not yet being assigned, the molecule was chosen because it consists of not only interesting but also possibly challenging structural motifs. Especially the spiro bicyclic motif is envisioned to be challenging to analyze, although similar elements are common in natural products.



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Selective On-Surface Synthesis of Isokekulene Facilitated by Strong Molecule-Substrate Interaction

Qitang Fan,[1] Anja Haags,[2] Alexander Reichmann,[3] Simon Werner,[1] Larissa Egger,[3] Hans Kirschner,[4] Tim Naumann,[1] Jose Martinez-Castro,[2] Felix Lüpke,[2] François C. Bocquet,[2] Christian Kumpf,[2] Serguei Soubatch,[2] Alexander Gottwald,[4] Georg Koller,[3] Michael G. Ramsey,[3] Mathias Richter,[4] Jörg Sundermeyer,[1] Peter Puschnig,[3] F. Stefan Tautz,[2] J. Michael Gottfried,[1] and Sabine Wenzel[1,2]

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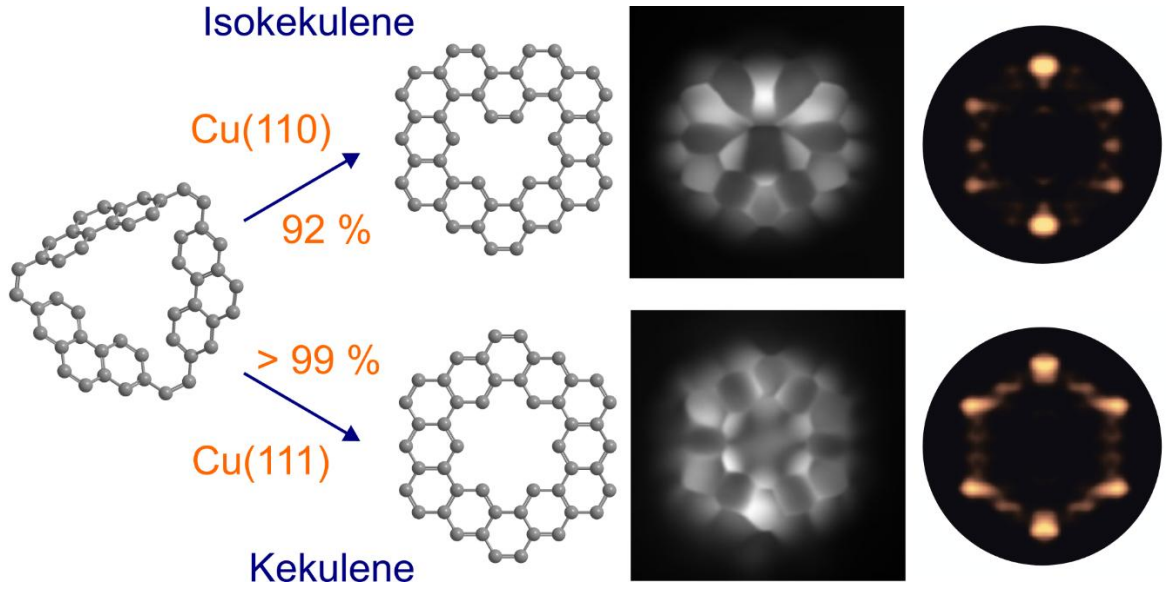
The role of different facets of metal nanoparticles in steering reaction pathways is crucial for the design of heterogeneous catalysts with superior selectivity. Transition-metal-catalyzed C-H bond activation is a widely applied strategy in the synthesis of various chemical compounds. Here, we report orthogonal selectivity in intramolecular cyclodehydrogenation of a nonplanar cyclic precursor steered by different facets of a copper single crystal. On Cu(110), the previously unknown cycloarene isokekulene is formed with a high selectivity of 92 %, while the same precursor on Cu(111) is known to react to form kekulene (> 99 %). Using scanning tunneling microscopy with CO-functionalized tips in combination with density functional theory (DFT) calculations, we identify two distinct adsorption geometries of the precursor which react to the respective products. The isokekulene molecule adopts two nonplanar adsorption configurations and exhibits strong molecule–substrate interactions, including significant charge transfer. These interactions are corroborated on a larger scale by photoemission orbital tomography. Overall, the enhanced molecule–metal interaction accounts for the more favorable energetics of isokekulene on Cu(110).



Tailoring on-surface polymerization by molecular coverage through indenyl coupling

(Poster contribution)

Alba García Frutos [1], Kalyan Biswas [1,4], Jesús Janeiro [2] Marco Lozano [3], Ana Barragán [1], Berta Álvarez [2], Diego Soler-Polo [3], Koen Lauwaet [1], José M. Gallego [1], Dolores Pérez [2], Rodolfo Miranda [2], José I. Urgel[1], Pavel Jelínek[3], Diego Peña [1,] David Écija[1]

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Indenyl coupling refers to the reaction where molecular precursors equipped with indenyl ligands promote the formation of C-C bonds, thanks to deprotonation of indenyl groups and subsequent homocoupling. This leads to extended π- conjugated polymers along a polyacetylene backbone, expanding the electronic delocalization.[1]

In this work, we present an on-surface chemical reaction in ultra-high vacuum conditions based on the regio- and stereo-selective covalent coupling of indenyl moieties[1] for fabricating π-conjugated systems whose dimensionality is directly driven by the initial molecular coverage of the precursor on the surface. The deposition of a dicyclopentaanthracene species (**1**) on Au(111) and its subsequent post-annealing at 150ºC leads to the controlled formation of various π-conjugated polymers. When the coverage is low (less than 0.3 ML), 1D chains with –syn and –anti bonding connections emerge (**2**). If the molecular coverage is around 0.5 ML, 1D extended zipper-like polymers are obtained (**3**). Finally, at very high coverage (almost 1 ML), small 2D patches are observed (**4**), whose size can be promoted by long annealing. By using scanning tunneling microscopy and non-contact atomic force microscopy, complemented by density functional theory simulations, the structural and electronic properties of the distinct polymers were rationalized. Notably the termini of the polymers are always doubly-hydrogenated as displayed in Figure 1. In addition we observe bandgaps of 3,2 eV for 1, 2,03 eV eV for 2 and 3,5 eV eV for 3, respectively. Our results open avenues for the controlled design of molecular nanoarchitectures on surfaces, while exploiting a recently discovered reaction at interfaces, the indenyl coupling.

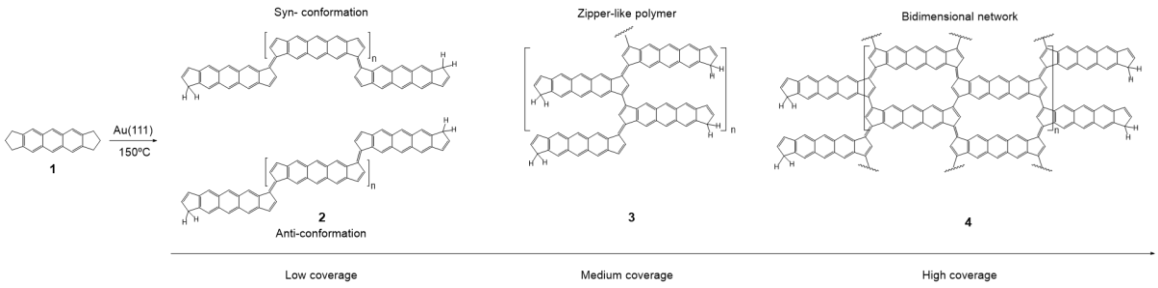

Figure 1. Dependence of the degree of polymerization on the molecular coverage.

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On-surface Synthesis of Aza-Coronoids

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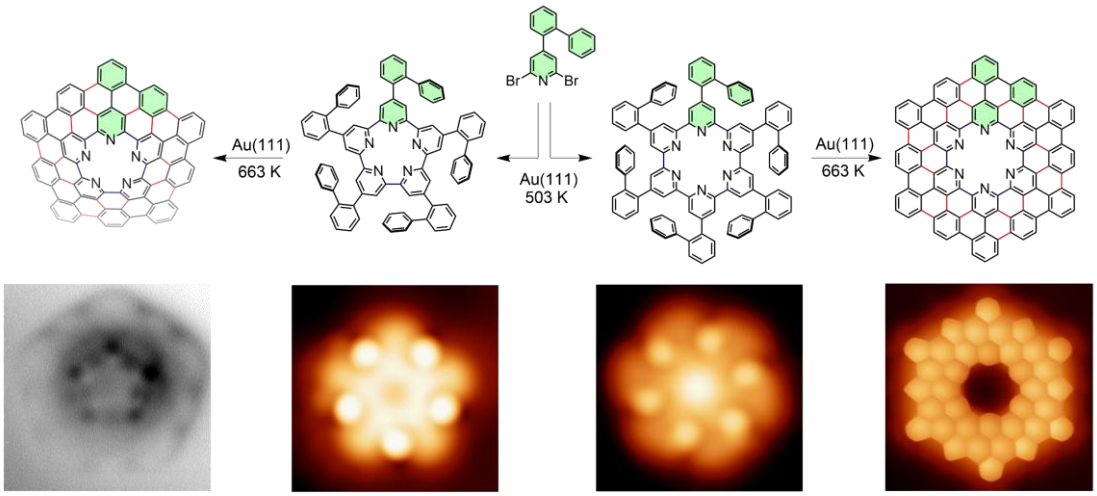
The electronic and magnetic properties of nanographenes can be tailored by altering the topology, introducing defect sites like vacancies, or doping with heteroatoms.[1] Coronoids represent a versatile sub-class of the nanographenes and can be regarded as benzenoids featuring a cavity. Synthesis by on-surface techniques has shown to be a promising approach, while in-solution synthesis of extended coronoid systems is challenging due to their low solubility.[2] To overcome this limitation, we combined in-solution and on-surface techniques, to gain access to various azacoronoids. The employed precursor molecules are derived from the same basic framework and possess a dibrominated pyridyl-functionality. By modification of their substituents, edge termination and conformation of the formed coronoids can be controlled. Besides planar armchair-edge and zigzag-edge terminated coronoids, a curved coronoid was synthesized. Nitrogen functionalization of the inner cavity allows for hosting a metal atom, giving rise to the formation of coronoid-metal complexes. The electronic and geometric properties of the nanostructures were investigated by low-temperature scanning tunneling microscopy/spectroscopy (STM/STS) and non-contact atomic force microscopy (nc-AFM).



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Theoretical investigation of 3,3”-dibrom-p-Terphenyl on copper Substrate

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Chemoselectivity is a key parameter for building customized organic nanostructures via bottom-up approaches. Therefore, strategies are needed that allow connecting molecular entities at a specific stage of the assembly process in a chemoselective manner. Studying the mechanisms of such reactions is the key to manipulate organic nanostructures on surfaces [1]. In particular, the knowledge about the precise adsorption geometry of intermediates at different stages during the reaction process and their interactions with surface atoms or adatoms is of fundamental importance. In this contribution, we determine the adsorption geometry of the 3,3”-dibrom-p-terphenyl as well as adsorbed mono/diradicals and the halogens from first-principles. The initially adsorbed molecules linked through C-Cu-C bonds are found in configurations consisting of long, chain-like and few shorter ring-like structures. With the progression of the reaction, the configurations show a shift from long chains to 3-molecule ring structures. For further comparability with experimental results, reaction paths and minimum energy barriers have been calculated by the Nudged Elastic Band (NEB) [2] methods for transitions between the observed linear chain and ring structures.

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Autonomous manipulations of non-planar molecules in STM

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Main text: Scanning tunneling microscopy (STM) has shown great promise in manipulating atoms or molecules in on-surface molecular synthesis. However, the selection of proper parameters for various manipulations requires extensive exploration and strongly depends on domain knowledge. To address this problem, we developed an algorithm to automate dissociation (breaking C-Br covalent bond) and movement (moving intact molecules) of non-planar molecules Zn(II)-5,15-bis(4-bromo-2,6-dimethylpheny)porphyrin ($ZnBr_2Me_4DPP$) through learning manipulation parameters on both Au(111) and NaCl(100)/Au(111) in STM. Meanwhile, DFT calculations were applied to explore 3D configurations and reaction mechanisms in combination of STM images. This approach paves the way for the bottom-up assembly of large polymers based on the building blocks.

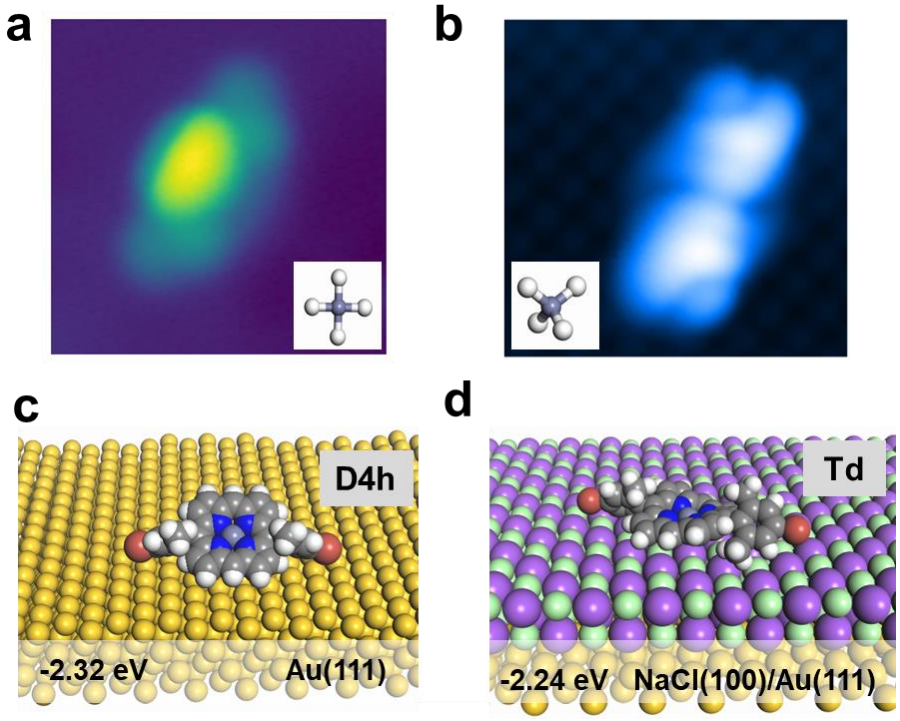

Fig 1. STM images and DFT-optimized 3D configurations of $ZnBr_2Me_4DPP$ adsorbed on Au(111) (a, c) and NaCl(100)/Au(111) (b,d).

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Ullmann coupling reactions on *NHC*-functionalized gold nanoparticles.

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The Ullmann reaction has been established as one of the oldest techniques for C-C formations of arylhalides, without the need for an additional organometallic species as a mediator.[1] Notwithstanding its valuable potential for atom economy, the reaction faces a major drawback in terms of the selectivity of homo over hetero-Ullmann reaction.[1] The notion of confining these reactions to transition metal surfaces has birthed the idea of on-surface syntheses, while transitioning the chemical environment from a typical three-dimensional reaction volume of solution phase synthesis to a seemingly two-dimensional platform.[2–4] With this new environment, alternative reaction pathways are created, and molecules can then be manipulated in the exact manner we wish them manipulated, resulting to not only high degrees of clear selectivities between homo and hetero-Ullmann products, but also providing access to new organic moieties which remain elusive via in-solution organic syntheses.[2,3–5] Nevertheless, this smart technique requires organic precursors to be deposited under ultra-high vacuum (UHV) conditions and onto highly defined single crystalline flat surfaces - to enable visualization with Atomic Force Microscopy - giving rise to single molecules. Moreover, it is not suitable for bulk material syntheses, and the use of high molecular weight precursors as starting materials. To translate and expand the scope of on-surface syntheses from a flat 2D surface to a rough 3D surface, we devised a protocol for Ullmann coupling reactions on organic-inorganic hybrid materials using *NHC*-functionalized gold nanoparticles (AuNps) on a one-system hybrid material, functioning as the catalyst and reacting partner.This technique enables scalability of the obtained product, avoids UHV conditions and in turn, allows the use of varied high molecular weight organic precursors as starting materials - features which are all difficult to attain via the conventional 2D on-surface syntheses. Furthermore, the new devised method enables access to nanoparticles functionalized with a covalent organic network cover, thus, giving rise to a new surface, which in turn, opens a new area of organic materials.

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Spin and charge control of topological end states in chiral graphene nanoribbons

(Poster contribution)

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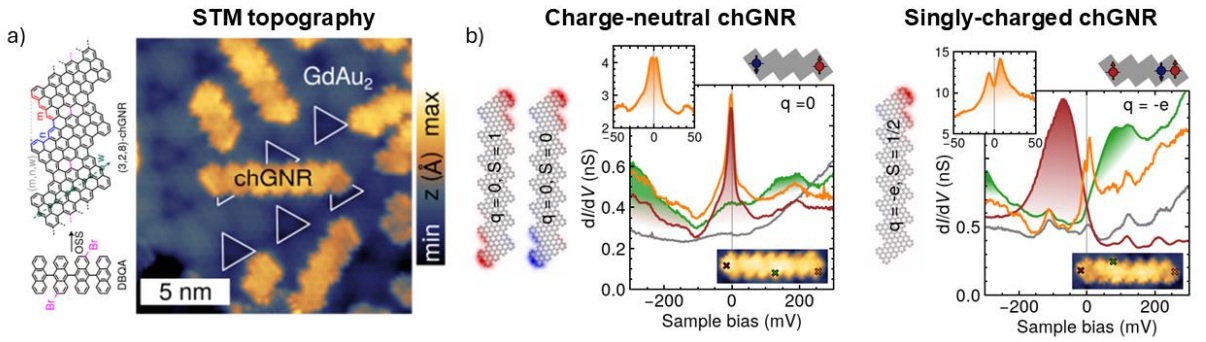
Two-dimensional surfaces formed by surface alloying of rare-earth and noble metals provide a unique platform for studying surface catalysis and magnetism.[1,2] A $GdAu_2$ monolayer on Au(111) catalyzes polymerization via Ullmann coupling and exhibits ferromagnetic ordering below 19 K with strong easy-plane anisotropy.[3] We use $GdAu_2$ as a substrate, prepared by evaporating Gd onto hot Au(111), to stabilize the spin polarization of synthesized (3,2,8)-chiral graphene nanoribbons (chGNRs) of varying lengths, enabling the exploration of magnetism in low-dimensional systems. We identify two distinct classes of chGNRs: those that are charge-neutral with unquenched singly occupied π-radical sites and those that are singly charged double occupied, as probed by scanning tunneling spectroscopy (STS) at 5K. Furthermore, we demonstrate a reversible transition between single and double occupancy or one charge state to another by laterally manipulating the chGNR along the substrate's moiré lattice using the STM tip, attributed to variations in the local work function of the substrate. Charge redistribution is further verified via Kelvin probe force microscopy (KPFM). Additionally, the chGNRs experience an effective magnetic field (B_{eff}) on different adsorption sites due to exchange bias with the underneath ferromagnetic substrate, which manifests as low-energy inelastic features in STS.



a) On-surface synthesis of chGNR on $GdAu_2$ surface. b) STS of two distinct chGNRs on different adsorption sites, describing charge neutral and singly charged chGNRs.

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Solution-Based Synthesis of Arene-Annulated Eight-Membered Carbo- and Heterocycles for On-Surface Studies

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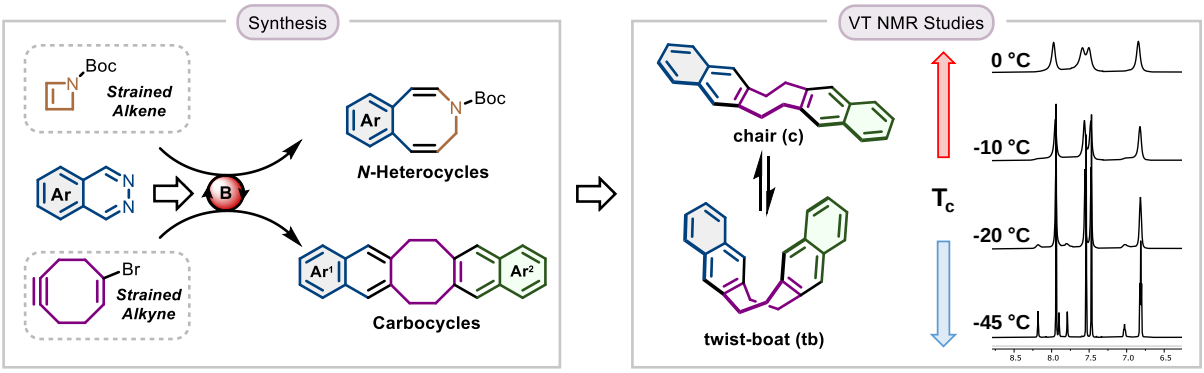
Owing to their distinctive conformational and electronic features, eight-membered carbo- and heterocycles are of fundamental importance in materials science. They have received significant attention in organic electronics,[1,2] polymer science[3] and chemical sensing.[4] In solution or in the solid state, these medium-sized rings can impart curved or saddle-shaped geometries into larger molecular frameworks.[5] However, constraining these structures to a two-dimensional surface can enforce planarization, giving rise to new electronic characteristics or reactivity patterns.[6,7] To enable the systematic study of surface-confined non-hexagonal rings, we developed a modular, solution-based approach for the synthesis of arene-annulated eight-membered carbo- and heterocycles from readily available phthalazines via Lewis acid catalysis. While variable temperature (VT) NMR studies gave insight into the conformational dynamics of the synthesized cyclooctadienes in solution, we envisage utilizing these compounds as precursors to investigate the on-surface behavior of strained, eight-membered ring systems.



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Heisenberg S-1/2 antiferromagnetic molecular chain

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Carbon-based molecular systems are emerging as promising candidates for realizing low-dimensional quantum spin models due to their intrinsic tunability and weak spin-orbit coupling. [1-2] However, the realization of prototypical spin-1/2 Heisenberg chain within such systems remains both experimentally and theoretically challenging. In this work, we present a theoretical investigation of finite Heisenberg spin-1/2 antiferromagnetic chains realized through the on-surface synthesis of diazahexabenzocoronene chains on Au(111). [3] Each molecular unit hosts a localized spin-1/2, and covalent coupling between neighboring units results in a well-defined antiferromagnetic exchange interaction. Using a combination of spin-polarized density functional theory, mean-field Hubbard modeling, and dynamic spin correlator calculations, we quantitatively capture the spin excitation spectra and parity-dependent phenomena observed in scanning tunneling spectroscopy (STS) measurements. Even-numbered chains exhibit gapped singlet-triplet excitations, while odd-numbered chains feature zero-bias Kondo resonances with site-dependent intensity, consistent with the formation of collective many-body ground states. Theoretical estimation of the nearest-neighbor exchange coupling yield $J \approx 30$ meV, attributed mainly to superexchange interactions intrinsic to the molecular framework, rather than substrate-mediated mechanisms. Dynamic spin correlator accurately reproduces the spatial distribution and spectral features of the STS conductance maps, providing a direct comparison with experimental observations. These results establish a theoretical basis for understanding spin excitations in molecular Heisenberg chains and highlight the potential of tunable molecular systems for exploring quantum mechanism, paving the way for engineered spin coherence and topological spin lattices in organic quantum materials.

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On-Surface Synthesis and Characterization of Long Azaacenes

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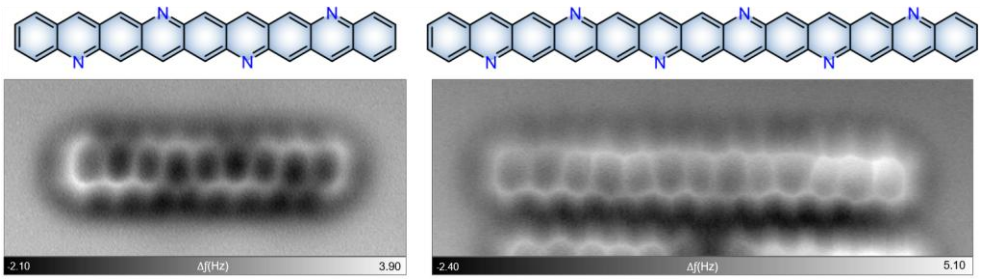
Introducing electronegative nitrogen atoms into the backbone of acenes yields azaacenes, which enables fine-tuning of the energy alignment of frontier orbitals and enhances resistance to oxidation and photodimerization. Azaacenes and their derivatives have been among the leading organic semiconducting materials for decades. However, a comprehensive understanding of their fundamental properties requires extending the homologous series toward longer azaacenes. Here, we demonstrate the on-surface synthesis of tetraazanonacene and hexaazatridecacene, the latter being the longest azaacene reported to date, 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 resulting azaacenes were characterized using a combination of scanning tunneling microscopy/spectroscopy (STM/STS) and non-contact atomic force microscopy (nc-AFM). For tetraazanonacene, we observe an increased frontier orbital gap compared to pristine nonacene, attributed to a more pronounced downshift of the occupied states. In the case of hexaazatridecacene, an open-shell singlet ground state is identified, with a singlet–triplet energy gap of 110 meV, which is slightly smaller than that observed for long regular acenes.



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Thermally Induced Skeletal Rearrangement of Polycyclic Conjugated Hydrocarbons: A Pathway to Novel Nanostructures

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On-surface synthesis offers a promising route for designing novel materials beyond traditional solution-based reactions. The final product's structure depends on the reaction mechanism of the precursor upon sublimation onto a selected surface. For instance, ring-rearrangement reactions are garnering interest, although controlling them remains challenging due to the numerous possible pathways. Here, we demonstrate that polycyclic conjugated hydrocarbon precursors equipped with gem-dibromide functional groups undergo a unique skeletal rearrangement when deposited on a hot Au(111) substrate. Such reaction contrasts with the intermolecular polymerization observed when the species are deposited at room temperature, followed by substrate annealing [1–4]. Scanning tunneling microscopy and non-contact atomic force microscopy reveal the formation of antiaromatic subunits, underscoring the potential of controlled ring-rearrangement reactions for engineering electron-rich, low-dimensional materials for molecular optoelectronics [5,6].

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Surface influences on the molecule identification via fingerprint extraction

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Atomic force microscopy (AFM) is a standard tool to gain access to the internal structure of a molecule. By determining the force exerted by the molecule on the AFM tip at a set height, the shape of atoms and bonds can be visualized. As the measurement is performed at constant height, this works well for flat molecules. However, the interpretation can become more difficult if the molecule has some amount of corrugation, or if it is not adsorbed parallel to the surface. Furthermore, identifying the species of the atoms without prior knowledge is a task which is very difficult to the human eye. Recently Pèrez *et al*. introduced a machine learning tool which interprets 3d stacks of constant height AFM images to derive the chemical formula of the molecule.[1] While the algorithm was trained with isolated molecules in the gas phase, it might also be able to handle medium corrugations of the molecule due to the interaction with the surface.

We study the influence of such surface effects to the molecule identification algorithm with 6Fluor-Pentacene as a test-molecule adsorbed to different surfaces. We test AFM images simulated via density functional theory (DFT) and the probe-particle method[2] as well as experimentally determined images. Furthermore we use the DFT data to gain a deeper insight in the adsorption characteristics and self-assembly of the molecule on those surfaces.

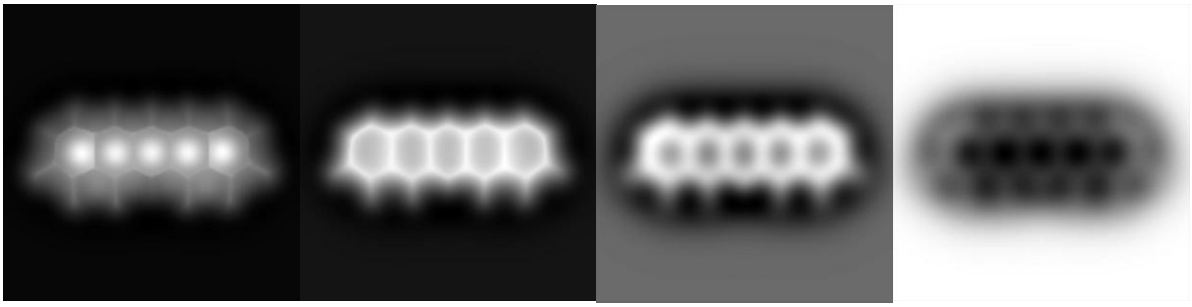

Figure 1: Simplified 3D stack of the 6Fluor-Pentacene in the gas phase

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Quasi-Planar π-Extended Cycloparaphenylenes: Computational Insights into On-Surface Synthesis and Electronic Properties

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Cycloparaphenylenes (CPPs), hoop-shaped conjugated macrocycles composed of para-linked phenyl rings, have attracted interest due to their curved aromatic systems and para-conjugation, which give rise to unique (opto-)electronic properties. Planarization of their π-electron systems is not possible, as it would further increase the inherent strain. However, partial planarization can be induced by incorporating suitable bending groups.

We report on computational insights using density functional theory (DFT) calculations[1] into the on-surface synthesis of quasi-planar π-extended [2n]CPPs (n=8-11) on Au(111) and their characterization via scanning tunneling microscopy/spectroscopy (STM/STS).[2] These π-extended CPPs are macrocycles with para-connected phenylenes forming the inner backbone.

While the n=8 CPP adopts a planar geometry on the surface, the n=9 to n=11 CPPs remain nonplanar upon adsorption. However, partial planarization due to dispersion interactions with the substrate enhances p-orbital interactions, leading to a decreasing trend in the HOMO-LUMO gap. This behavior resembles that of forced planar CPPs and contrasts with conventional nonplanar CPPs, demonstrating their quasi-planar character. Furthermore, π-extension results in a reduced gap compared to the unsubstituted planar parent [2n]CPP. dI/dV maps reveal electronic orbital confinement at the edges and fjord regions, attributed to slower wave function decay. The nonplanar perylene groups in the larger CPPs affect this orbital confinement, altering the appearance of the fjord regions of planar n=8 CPP and quasi-planar n=9 to n=11 CPPs.

The unprecedented CPPs presented here provide a valuable platform for systematic and fundamental studies into their physicochemical properties, offering new insights into the interplay between planarity, π-conjugation, and electronic structure in strained aromatic systems.

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On-Surface Synthesis and Reactivity of Biphenylene Network on Au(788)

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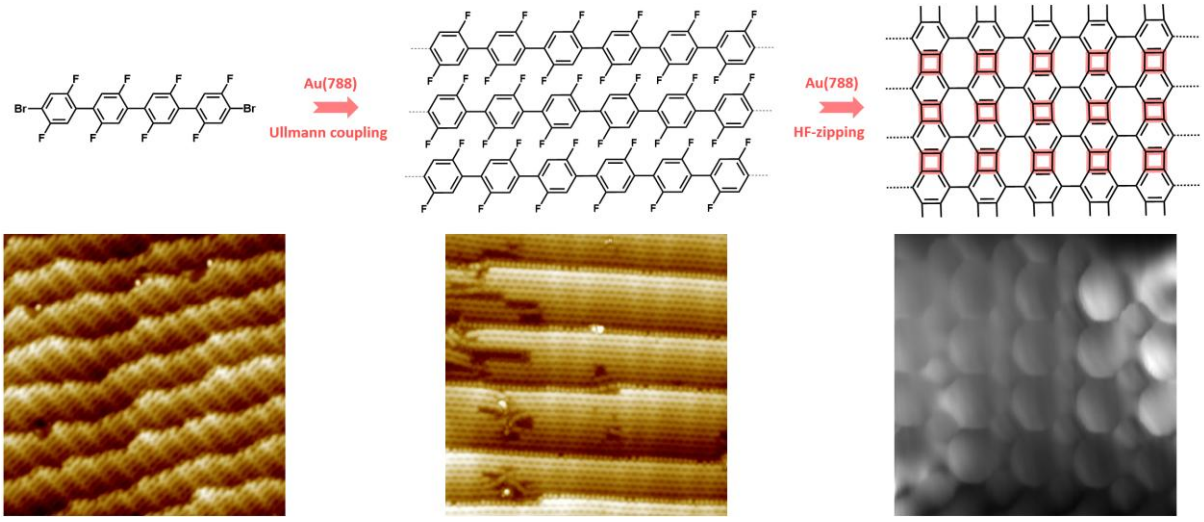
The recently synthesized biphenylene network (BPN)[1], a new sp^2-hybridized carbon allotrope comprising four-, six-, and eight-membered rings, significantly differs from graphene in its electronic and chemical properties. Theoretical studies predict that BPN features a multiradical ground state, with its open-shell character predominantly localized at the four-membered rings[2]. However, experimental confirmation of these predictions has been hindered by the limited quality of the material currently available. To address this challenge, we employed Au(788), a surface characterized by narrow terraces, and designed an extended molecular precursor to promote the formation of the desired structure. For comparison, we also investigated interpolymer dehydrofluorination (HF-zipping) reactions of the precursor on Au(111). Scanning probe microscopy (SPM) analysis revealed that pure BPN fused chains formed on Au(788) exhibit superior structural quality compared to those synthesized on Au(111). These findings provide a solid experimental foundation for probing the theoretically predicted properties of BPN, opening avenues for the further exploration of its distinctive electronic and chemical behavior.



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Computational Study of Ullmann Coupling Reaction of Bromobenzene on the Coinage Metal Surfaces

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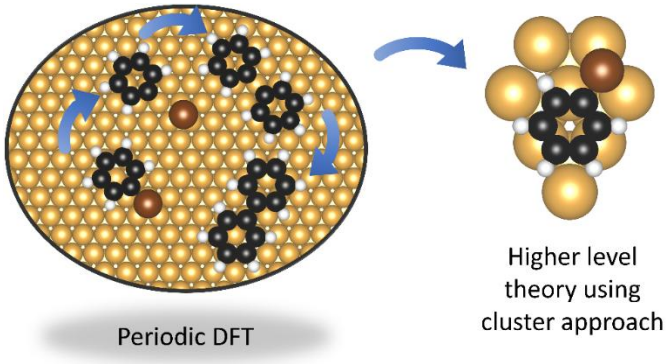
Experimental studies of the on-surface Ullmann coupling reaction on the coinage metal surfaces have gained increasing interest in recent years, as it provides a promising path to *e.g.* 2D graphene-like structures, while allowing for a high flexibility with concern to the product. To rationalize experimental findings, density functional theory (DFT) methods are mainly used. However, a variety of combinations of different exchange-correlation functionals and dispersion corrections often make the results of the calculations controversial [1,2].

The different steps of the Ullmann coupling reaction were investigated using 22 XC-functionals and 5 dispersion corrections on the Cu(111), Ag(111), and Au(111) metal surfaces with periodic boundary conditions. A pre-selection was made by calculating the bulk lattice parameters and the structure of bromobenzene before a more detailed study of the energy and structural parameters of the reaction steps was carried out [3].

The computed adsorption energies and the adsorbate–surface distances were analysed in detail. To predict the structure and energy of the adsorbed chemical systems, various DFT approximations were benchmarked against correlated *ab initio* MP2 and CCSD(T) methods using a cluster approach [3].

Further, in cooperation with experimentalists, a comparison of the D3(BJ) and the D4 dispersion corrections was performed for large organic compounds on a Au(111) surface by means of adsorption energy and structure.



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Relating Radical Delocalization, Charge Transfer and Magnetic Ground State in Acene-Derived Oxyradicals

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Recent progress in vacuum-based on-surface synthesis has greatly advanced our ability to engineer open-shell carbon materials, in line with the growing interest in π-magnetism for future electronic and spintronic technologies [1]. However, the interplay between electronic structure descriptors and open-shell character remains poorly understood. Herein, we propose a facile synthesis of open-shell acene-derived oxyradicals and demonstrate the critical effect of substrate-induced charge transfer on their magnetic ground state. Through a systematic comparison, we reveal how the type, number, and distribution of functional groups -as well as radical delocalization- influence the presence or absence of interfacial charge transfer, ultimately modulating the molecule's π-magnetism. This work provides valuable insights into the interdependence of electronic descriptors and magnetic behavior, contributing to the rational design of molecular materials with tailored functionalities.

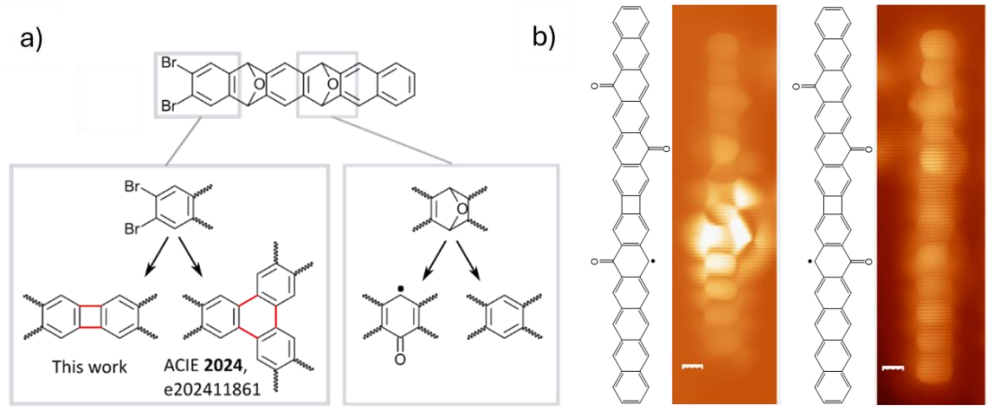

Figure. (a) Precursor molecule with halogen (left) and epoxy (right) functionalization. Upon annealing, halogens induce intermolecular coupling (red), while epoxies either convert to carboxy groups with radicals or cleave off. (b) Schematic representation of two hexacene dimer derivatives bearing carbonyl groups at different positions, alongside their corresponding STM images.

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Precursor synthesis for nitrogen doped graphene nano structures

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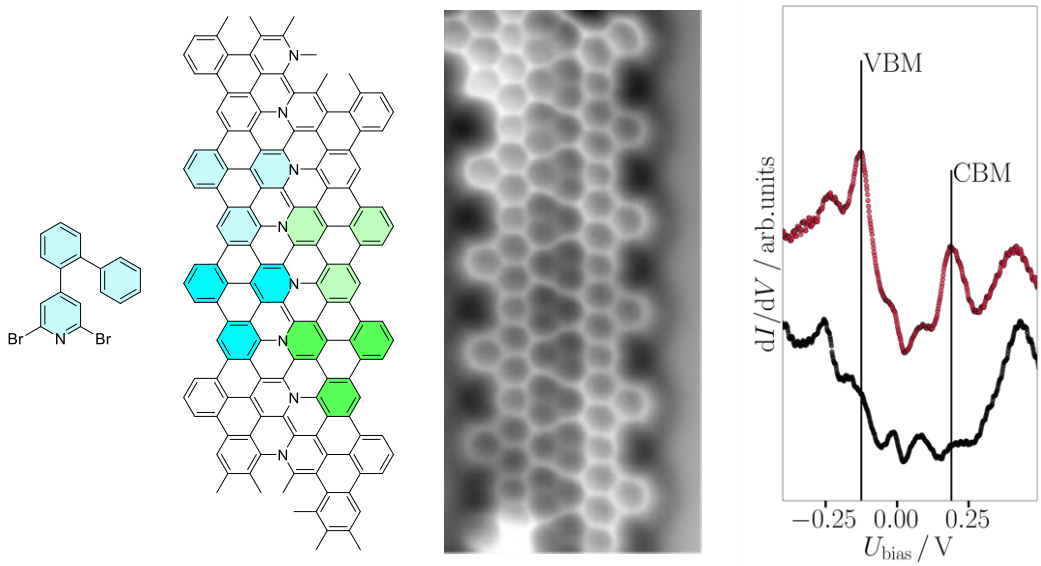
Tuning the electronic properties in carbon nano structures is a precondition to use them for application in semiconductors[1], organic electronics[2] and solar cells[3]. The properties can be altered by doping with heteroatoms like nitrogen. In comparison to the purely hydrocarbon derivatives, the electron-count of the nano graphene increases by one per nitrogen atom, when the nitrogen atom with coordination number three is embedded in the carbon backbone. Such a graphitic nitrogen partially contributes its additional electron to the π-system.[4] Outgoing from the employed precursor molecule, its connectivity allows formation cyclic products, where the pyridinic nitrogen points towards the cavity. Furthermore, linear products with graphitic nitrogen atoms are observed on the Au(111) surface. The nitrogen atoms which are incorporated in the center of the ribbon show in the constant height AFM (CH-AFM) image a lower contrast in comparison to the carbon atoms, indicating a lower adsorption height. STS shows no zero bias resonance but a significant reduction of the band gap, which is with 0.3 eV very low. This makes the material unstable with respect to oxidation[5]. From these results alternative precursors were designed and synthesized, which could provide access to nitrogen embedded nano structures exclusively.



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On-Surface Synthesis of (1,3)-chGNRs with Five-Membered Ring Edge Extensions

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Graphene nanoribbons (GNRs) exhibit highly tunable electronic properties, making them promising candidates for next-generation nanoelectronic and optoelectronic devices. Precise control over their atomic structure, including width, crystallographic symmetry, heteroatom doping, and edge termination, is crucial for tailoring their electronic behavior.

Here, we introduce a novel strategy for the edge functionalization of (3,1)-chiral graphene nanoribbons (chGNRs) [1] by incorporating five-membered rings into their backbone. Using 2,2′-dibromo-9,9′-bianthracene precursors equipped with alkyne groups, we induce selective ethynylarene rearrangement via on-surface cycloaddition, leading to the formation of cyclopenta-fused polycyclic aromatic hydrocarbons at the nanoribbon edges. High-resolution scanning tunneling microscopy (STM) and atomic force microscopy (AFM) reveal the integration of five-membered rings in both ortho- and para- configurations, significantly modifying the chGNRs' electronic structure. This approach demonstrates a new avenue for structural and electronic engineering of GNRs.

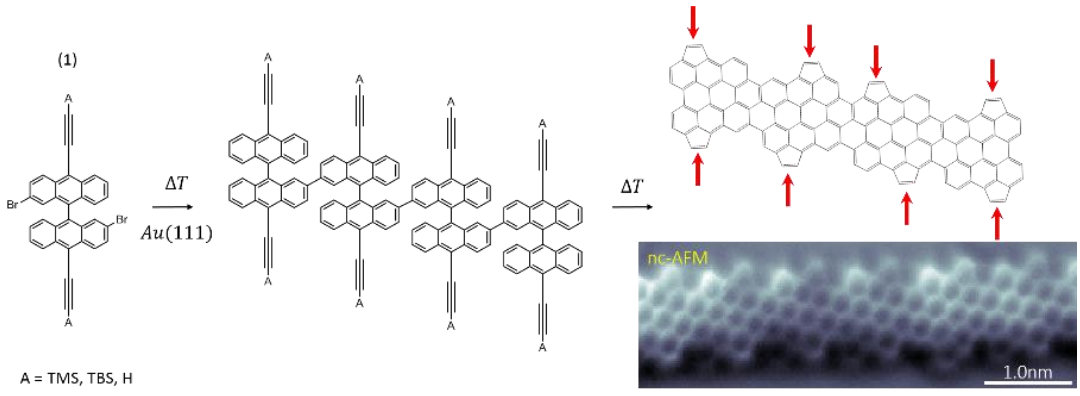

Figure – Scheme of the reaction including the molecular precursor (1), polymerization and cyclization. Constant height high-resolution nc-AFM image with a CO-decorated tip of the edge extended chiral graphene nanoribbon.

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Theoretical Investigation of Dibromopyrene and Iodotriphenylene on Sodium Chloride Coated Copper Substrate

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Organic 2D materials are of great interest for various applications in molecular electronics. Increasingly sophisticated methods of on-surface manipulation via probe tips extend the scope of possible structure modifications to tune the (electronic) properties of such nanostructures.

Halogenated organic precursors such as Dibromopyrene (DBP) and Iodotriphenylene (IT) are the building blocks for the assembly of more complex structures. A sodium chloride bilayer helps to electronically decouple the metallic Cu (1 1 1) substrate from adsorbates, increasing mobility and thus simplifying manipulation.

The Vienna Ab initio Simulation Package [1] implementation of density functional theory is used to calculate potential energy surfaces and nudged elastic bands for modelling adsorption behavior and diffusion pathways, respectively. For both DBP and IT, physisorption and a strong halogen-surface interaction can be identified as adsorption mechanism. The resulting adsorption geometries are in great accordance with experimental findings [2]. Both molecules show high mobility with energy barriers an order of magnitude smaller than their adsorption energies.

Further comparability with experimental results is achieved by simulation of atomic force microscopy imaging using the Probe-Particle Model [3].

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Temperature Induced On-Surface Ring-Opening Polymerization Reaction for the Synthesis of Nanoribbons: Strain Influence of Cycloparaphenylenes

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In on-surface synthesis (OSS), many reactions are performed via an Ullmann-type reaction step, involving halogenated precursors. However, in the reaction steps, cleaved halogen adatoms might disturb the interaction of intermediates and product formation. Therefore, there is a growing demand for halogen-free precursors when performing on-surface reactions. Recently, we found that halogen-free [6]Cycloparaphenylene ([6]CPP) is suited to thermally induce a ring-opening polymerization (ROP) to synthesize graphene (GNR) and biphenylene nanoribbons (BNR) via undisturbed formation of ordered poly(*para*-phenylene) chains. [1] However, the mechanism of this reaction and the use of CPP's as precursors in OSS is not well understood yet. In this study, we investigate the strain influence of a set of Cycloparaphenylenes of different sizes (namely [6]CPP, [8]CPP and [10]CPP). [2] Our results suggest that the ROP is facilitated when performing the ROP with smaller, highly strained CPP's such as [6]CPP. For larger CPP's with lower strain energies the initial ring opening is hampered, leading to only partial polymerization for [8]CPP and no polymerization in the case of [10]CPP. Furthermore, dehydrogenation of individual phenyl rings in intact CPP rings is observed in case of [8]CPP and [10]CPP which hinders polymerization.

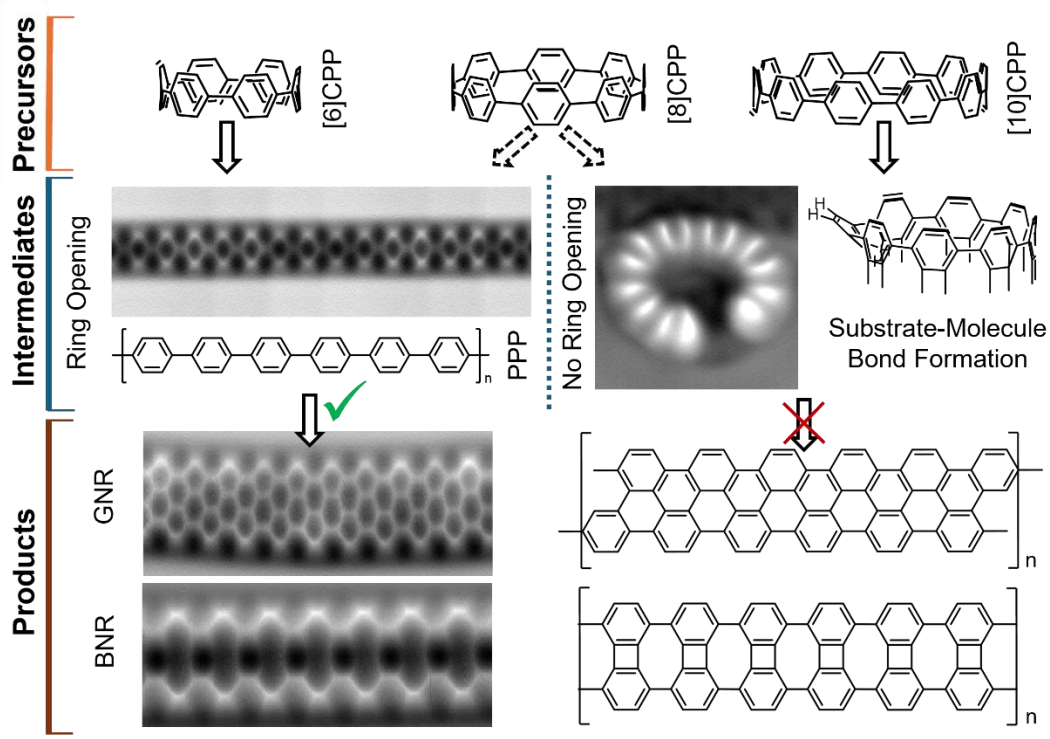

Figure 1. Reaction path of the ROP of CPP's. A full polymerization is observed for [6]CPP, whereas for [8]CPP and [10]CPP only partly or no polymerization reaction is observed.

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