

**“Molecular Functionality at Surfaces:
Self-Assembly, Manipulation,
Reactivity and the Role of Decoupling”**

747. WE-Heraeus-Seminar

30 October - 04 November 2022

hybrid

at the Physikzentrum Bad Honnef, Germany

**WILHELM UND ELSE
HERAEUS-STIFTUNG**



Introduction

The Wilhelm und Else Heraeus-Stiftung is a private foundation that supports research and education in science with an emphasis on physics. It is recognized as Germany's most important private institution funding physics. Some of the activities of the foundation are carried out in close cooperation with the German Physical Society (Deutsche Physikalische Gesellschaft). For detailed information see <https://www.we-heraeus-stiftung.de>

Aims and scope of the 747. WE-Heraeus-Seminar:

The emergence of organic materials in current and future applications like displays, sensors, separation techniques, electronics or in energy storage is driven and fueled by the virtually unlimited synthetic possibilities for tailoring their electronic, chemical, optical and (photo-) catalytic properties. For the performance of organic materials in (key) applications, not only the molecular structure of the organic materials, but also interfaces to inorganic materials play vitally important roles. Fundamental insight into the properties of organic materials confined at these interfaces is gained from studying both individual molecules and molecular structures on surfaces in defined environments by taking full advantage of highly resolving surface-sensitive techniques, foremost scanning probe microscopy. On the one hand, these model environments reduce complexity by reducing the dimensionality due to the usage of flatlands. On the other hand, molecule-surface interactions affect both structure formation and properties of the adsorbed species.

For understanding the interplay of the different interactions, the close collaboration between experimentalists and theoreticians is essential for advancing the field and will be reflected in the seminar. An overarching goal of this seminar is to present and discuss the disparate research trends of supramolecular selfassembly, on-surface synthesis, decoupling and controlled manipulation of single molecules or molecular nanostructures alongside. One mission is to identify similarities, distinguish technical from principal differences and utilize synergies within the field, also to other closely related research fields on organic materials.

Scientific Organizers:

Prof. Dr. Sabine Maier	Universität Erlangen-Nürnberg, Germany E-mail: sabine.maier@fau.de
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Introduction

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Registration:

Elisabeth Nowotka (WE Heraeus Foundation)
at the Physikzentrum, reception office
Sunday (17:00 h – 21:00 h) and Monday
morning

Program

Program

Sunday, 30 October 2022

17:00 – 21:00 Registration

18:00 *BUFFET SUPPER and informal get-together*

Monday, 31 October 2022

08:00 *BREAKFAST*

08:50 Scientific organizers **Welcome**

09:00 – 09:45 William Dichtel **Two dimensional polymers and polymerizations**

09:45 – 10:30 Steven De Feyter **Formation and functionalization of 2D materials: a molecular approach**

10:30 – 11:00 *COFFEE BREAK*

11:00 – 11:45 Steven Tait **Supramolecular self-assembly and metal-ligand redox assembly at surfaces**

11:45 – 12:30 Angelika Kühnle **Structural transitions of molecules on surfaces**

12:30 – 12:50 **Conference Photo** (in the front of the lecture hall)

12:50 – 14:00 *LUNCH*

Program

Monday, 31 October 2022

14:00 – 14:45	Junfa Zhu	Chiral nanostructures constructed via on-surface chemistry
14:45 – 15:30	Giovanni Costantini	Primary and secondary structure of conjugated polymers uncovered by ESD-STM
15:30 – 16:00	<i>COFFEE BREAK</i>	
16:00 – 16:45	Christian Wäckerlin	In-situ ToF-SIMS as a tool to study on-surface synthesis: Unraveling the fates of atomic hydrogen
16:45 – 17:30	Milica Todorovic	Bayesian inference of surface adsorbates
17:30 – 17:45	Stefan Jorda	About the Wilhelm and Else Heraeus Foundation
18:30	<i>DINNER</i>	

Program

Tuesday, 01 November 2022

08:00	<i>BREAKFAST</i>	
09:00 – 09:45	Jascha Repp	Accessing non-equilibrium states at atomic scales
09:45 – 10:30	Pavel Jelinek	On-surface synthesis and SPM characterization of polyradical PAHs with strong multireference character
10:30 – 11:00	<i>COFFEE BREAK</i>	
11:00 – 11:45	Nacho Pascual	Magnetism in engineered graphene nanostructures
11:45 – 12:30	David Ecija Fernandez	On-surface synthesis of π-conjugated Polymers
12:30 – 14:00	<i>LUNCH</i>	
14:00 – 14:45	Reinhard Maurer	Dynamic charge-transfer at functional metal-organic interfaces: What is it and how can we control it?
14:45 – 15:30	Poster Flash I	
15:30 – 16:00	<i>COFFEE BREAK</i>	
16:00	Poster Session I	
18:30	<i>DINNER</i>	

Program

Wednesday, 02 November 2022

08:00	<i>BREAKFAST</i>	
09:00 – 09:45	Wilhelm Auwärter	Ring-closing reactions of porphyrins on noble metal surfaces
09:45 – 10:30	Ernst Meyer	Polymeric wires, nanoribbons and 2d-molecular networks studied by scanning probe microscopy
10:30 – 11:00	<i>COFFEE BREAK</i>	
11:00 – 11:45	Martin Sterrer	Control of charge transfer into organic molecules on surfaces
11:45 – 12:30	Christian Lotze	Molybdenum Disulfide on Au(111) – growth, electronic structure and versatile playground for single molecule spectroscopy
12:30 – 14:00	<i>LUNCH</i>	
14:00	Excursion	
18:30	<i>HERAEUS DINNER</i> at the Physikzentrum (social event with cold & warm buffet, with complimentary drinks)	

Program

Thursday, 03 November 2022

08:00	<i>BREAKFAST</i>	
09:00 – 09:45	Leonhard Grill	Molecular motion at surfaces
09:45 – 10:30	Francesca Moresco	Dual functionality of single molecule machines: Rotors and nanocars
10:30 – 11:00	<i>COFFEE BREAK</i>	
11:00 – 11:45	Daniel Ebeling	Towards understanding and controlling on-surface coupling reactions and self-assembly mechanisms
11:45 – 12:30	Jonas Björk	Studying surface-confined reactions and decoupling of molecular structures from theoretical modeling
12:30 – 14:00	<i>LUNCH</i>	
14:00 – 14:45	Magali Lingenfelder	Hands up! Spin up! Chiral molecular layers controlling achiral electrocatalysis
14:45 – 15:30	Poster Flash II	
15:30 – 16:00	<i>COFFEE BREAK</i>	
16:00	Poster Session II	
18:30	<i>DINNER</i>	

Program

Friday, 04 November 2022

08:00	<i>BREAKFAST</i>	
09:00 – 09:45	Peter Beton	Light emission from molecular/2D hybrid van der Waals heterostructures
09:45 – 10:30	Shelley Claridge	Precision patterning of soft surfaces
10:30 – 11:00	<i>COFFEE BREAK</i>	
11:00 – 11:45	Guillaume Schull	Hyper-resolved fluorescence microscopy of molecular and extend systems
11:45 – 12:30	Organizers	Concluding remarks
12:30	<i>LUNCH</i>	

End of the seminar and departure

Posters

Poster session I

- Rajan Adhikari **Microscopic insight in the structure of an ionic liquid [C1C1Im][Tf2N] on Cu(111): An integrated experimental and theoretical investigation**
- Paula Angulo Portugal **Chemical sensing with CN-functionalized chiral graphene nanoribbons**
- Arash Badami Behjat **A highly drift stable low temperature STM based on a flow cryostat**
- Jia Baoxin **Bias-dependent switching of molecular nanostructures at the solid-liquid interface: the influence of concentration**
- Daniel Baranowski **Conservation of Nickel ion single-active site character in a bottom-up constructed π -conjugated molecular network**
- Richard Berger **Role of adatoms for the adsorption of F4TCNQ on Au(111)**
- Jonas Brandhoff **Effects of oxygen functionalization on the molecule-substrate coupling**
- Jan Patrick Calupitan **From open- to closed-shell character in molecular dimers of different coupling motifs**
- Yunjun Cao **Tuning the chirality change of a single molecule by van der Waals interactions**
- Binbin Da **On-surface assembly of graphyne-like networks on Ag(111) and Au(111)**
- Zhinan Fu **Electric-field induced 2D polymerization/depolymerization of boroxine-linked single-layer COFs at the solid/liquid interface**

Poster session I

Ilias Gazizullin	Adsorption and reactivity of organic molecules on the Cu(110)-(2×1)O striped phase
Elie Geagea	[4+4] photodimerization of triptycene derivatives with anthracene blades on ionic crystals
Afra Gezmis	Investigation of the wetting layer of [C1C1Im][Tf2N] on Pt(111) by variable temperature scanning tunneling microscopy
Maximilian Halbauer	Single-molecule mechanics: A nc-AFM and STM study of nonahelicene on Ag(110)
Ralf Hemm	Structural reorientation of organic molecules on surfaces by alkali metal doping
Lukas Höltkemeier	Non-equilibrium structures of C60 on CaF2(111)
Tianze Hu	From aperiodic to periodic self-assembly at the liquid-solid interface
Simon Jaekel	Self-assembly and thin film growth dynamics of an ionic liquid on Au(111) investigated in real space
Zdenek Jakub	Graphene-supported 2D metal organic frameworks with remarkable thermal and chemical stability: Ni-, Fe-, and Mn-TCNQ
Sven Johannsen	Spin switching in self-assembled tetramers on Ag(111)
Katharina Kaiser	Charge-state lifetimes of single molecules on ultrathin insulating films
Leonard-Alexander Lieske	Distance dependence of s- and p-wave contributions in CO-tip STM

Poster session I

Lacheng Liu

Polymerization of silanes via dehydrogenative Si-Si bond formation on metal surfaces

Benjamin Mallada

On-surface strain-driven synthesis of nonalternant non-benzenoid aromatic compounds containing four- to eight-membered rings

Ana Sanchez-Grande

Photoactivity of anhydrides on a semiconductor surface

Posters session II

Daniel Moreno	Tailoring electronic and magnetic properties of metal-organic coordination networks by lanthanide exchange
Stefania Moro	Interaction of a novel strong organic electron acceptor with Au(111): can SPM and DFT be enough to investigate the presence of adatoms in metalorganic frameworks?
Behzad Morteza pour	Phenyl- trioxatriangulenium on Au (111) studied with low-temperature scanning tunneling microscopy
Kaifeng Niu	Unveiling the formation mechanism of the biphenylene network
Youngwook Park	Plasmon-induced molecular manipulation of PTCDA on Si(111): An STM-TERS study
Vibhuti Rai	Pathway to achieve tunable single molecule light emitting sources
Bernhard Ramsauer	Autonomous single-molecule manipulation based on reinforcement learning
Shammi Rana	Surface-assisted and solvent dependent elimination of redox-active axial ligand of metal porphyrin
Massimiliano Remigio	Synthesis and chiral resolution of [2.2]paracyclophane derivatives on HOPG surface: Self-assembled monolayer of 3D nanostructure
Fran Romero-Lara	Synthesis and characterization of magnetic aza-triangulene nanostructures
Anna Roslowska	Funneling energy at the molecular scale

Posters session II

Karl Rothe	Atomic forces and relaxations in single-molecule reactions
Daniel Rothhardt	Local work function of graphene nanoribbons
Suchetana Sarkar	LT-STM induced reversible switching of thiophene based molecule on Au(111)
Alex Saywell	Molecular-substrate systems studied by scanning tunnelling microscopy: Spatial, energetic, and temporal resolution
Paul Philip Schmidt	Unusual diffusion and Island evolution in Pb/Si(111)-(7x7)
Bertram Schulze Lammers	Atomic-scale and electrochemical characterization of catalytically active triazine-based copper nitrides
Johannes Seibel	Visualization of D- and L-glycan assemblies and their interactions by high-resolution scanning tunneling microscopy
Hexia Shi	On-surface synthesis of nonplanar polymer chains containing oxygen functionalized pores
J. Rika Simon	Emergence of a singly-occupied state of p-terphenyl-based thiols bound to sulphur defects on MoS₂/Au(111)
Tao Wang	Aza-Triangulene and its fused dimers on surfaces
Tobias Weiss	Self-assembly and single-molecule manipulation of Borazine on Ag(111)
Linghao Yan	Fabrication and characterization of 2D metal-organic frameworks on weakly interacting 2D materials

Posters session II

Zhen Yao

Permeation through carbon nanomembranes

Ka-Man Yu

Exciton dynamics and electron delocalization in C60 thin films

Lihua Yu

Self-assembly behavior of molecules under confinement conditions

Abstracts of Talks

(in alphabetical order)

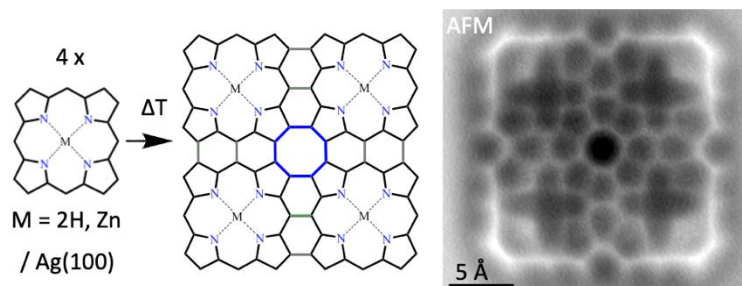
Ring-Closing Reactions of Porphyrins on Noble Metal Surfaces

W. Auwärter¹

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As nicely summarized in the description of this WE-Heraeus seminar, the molecular structure of organic materials, as well as interactions with the environment, play important roles for the resulting properties and functionalities. Specifically, on-surface chemistry protocols can provide access to distinct molecular structures at confining interfaces [1] and specific supports (including two-dimensional materials) can be applied to tailor molecular properties and to guide the self-assembly [2]. In this context, porphyrinoids represent versatile building blocks for self-assembled molecular films, metal-organic coordination networks, and covalent architectures at interfaces [3]. Here, I will mainly focus on temperature-induced ring-closing reactions of porphyrins on single crystalline Ag and Au surfaces in an ultrahigh vacuum environment, yielding individual molecules, one-dimensional oligomers, and two-dimensionally extended polyporphyrin systems. Specifically, the examples cover the formation of square-type porphyrin tetramers featuring a central antiaromatic cyclooctatetraene (COT) moiety (see figure), the assembly of porphyrin - graphene nanoribbon hybrids including benzenoid and non-benzenoid motifs [4], and the synthesis of π -extended oxygen-embedded porphyrins via O-annulation. The resulting products are characterized by scanning tunneling microscopy and bond-resolved atomic force microscopy. These experiments thus provide access to new porphyrin-based systems with distinct properties.

Additionally, I might provide a brief overview on our research activities employing atomically thin hexagonal-boron nitride films on metal supports as decoupling layers for individual molecules and molecular nanostructures.



References

- [1] L. Grill, S. Hecht, *Nat. Chem.* **12**, 115 (2020)
- [2] W. Auwärter, *Surf. Sci. Rep.* **74**, 1 (2019)
- [3] W. Auwärter *et al.*, *Nature Chem.* **7**, 105 (2015)
- [4] J. Deyerling *et al.*, *J. Phys. Chem. C* **126**, 8367 (2022)

Light emission from molecular/2D hybrid van der Waals heterostructures

T. James¹, J. Bradford¹, J. Kerfoot^{1,2}, S.A. Svatek^{1,3}, V.V. Korolkov^{1,2},
E. Antolin³, T. Taniguchi⁴, K. Watanbe⁴ A.S. Nizovtsev⁵, E. Besley⁵
and P.H. Beton¹

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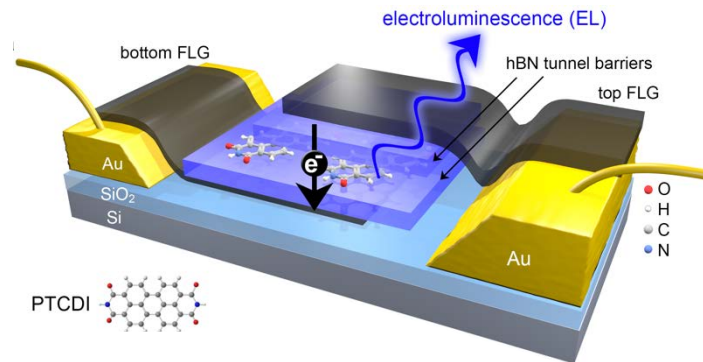
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Monolayer arrays of organic fluorophores can be deposited on the insulating hexagonal boron nitride (hBN) surface and the resulting photoluminescence is influenced by factors including van der Waals-induced deformation of molecular conformation, and the coupling of transition dipole moments with neighbouring molecules and the dielectric substrate. It is also possible to identify molecular arrays on exfoliated few-layer hBN flakes and integrate these layers into simple electrical devices in which a molecule monolayer is sandwiched between two hBN tunnel barriers which are, in turn, placed between two few-layer graphene electrodes. In these devices (shown schematically below) we observe electroluminescence from molecules excited by tunnelling electrons.



The electroluminescence exhibits up-conversion, i.e. the photon energy is greater than the energy, eV, gained by a tunnelling electron when a voltage V is applied across the device. This implies a multi-electron excitation process which we show is mediated by the formation of a triplet state. We compare devices formed by several different molecules and polymers. For some molecules we also observe emission from the triplet state and we discuss this emission and relate it to the alignment of molecular energy levels with Fermi energy in the contacts.

Studying surface-confined reactions and decoupling of molecular structures from theoretical modeling

J. Björk¹

¹Materials Design Division, Department of Physics, Chemistry and Biology, IFM, Linköping University, Linköping, Sweden

Studying chemical reactions on surfaces is fascinating from several aspects, both due to the two-dimensional environment reducing the degrees of freedom of molecules and the chemical reactivity a surface may have. For example, deposition of suitable molecular precursors can result in the formation of well-defined nanostructures which are difficult to obtain by conventional wet chemistry approaches. Furthermore, working under well-defined conditions, using ultraclean monocrystalline surfaces under ultrahigh vacuum, together with high resolution scanning probe microscopy and a variety of spectroscopic techniques, makes it possible to study the mechanisms of chemical reactions at a fundamental level. However, experiments are most often limited to provide information about reactants and products and sometimes intermediate states.

Theoretical modeling – in terms of density functional theory (DFT) – has become increasingly popular for studying the atomistic details of chemical reactions on surfaces. Here, the DFT-based methods for computationally studying molecules on surfaces will be presented, with particular attention to on-surface reactions. We will demonstrate the abilities of DFT to provide complementary support for the interpretation of experimental data as well as insights into actual reaction pathways. We will also discuss the decoupling of organic nanostructures. The intention is to give an overview of the information that theoretical modeling can provide but also some of the difficulties we need to have in mind. This will be achieved by focusing on systems of molecules undergoing chemical reactions on surfaces and the decoupling of molecular structures from surfaces.

Precision Patterning of Soft Surfaces

S. Claridge¹

¹*Purdue University, West Lafayette, Indiana, USA*

Many problems in modern materials chemistry require interfaces with highly structured chemical environments at near-molecular scales – ranging from nanoelectronics to ligand clustering in biology. For over a century, lipids have provided a powerful toolkit for controlling nanoscale interface chemistry, both for biology and for synthetic materials. Here, we describe the powerful chemical impacts of amphiphilic striped phases, which can be assembled on graphite, MoS₂, and other 2D materials. These unusual molecular layer structures provide surprisingly robust and scalable nm-resolution chemical patterning, which can direct further material assembly. Recently, we have also demonstrated that these patterns can be assembled on hard, crystalline 2D materials, then transferred to soft, amorphous materials including PDMS and hydrogels, creating new opportunities for nanostructured material design. We will discuss the relationship between structure, reactivity and assembly in the molecular template layer, as well as applications of the templates in directing the assembly of inorganic nanocrystals and in designed cell scaffolds for regenerative medicine.

References

- [1] J.J. Bang, *Journal of the American Chemical Society* **138**, 4448 (2016)
- [2] T.A. Villarreal, *Journal of the American Chemical Society* **139**, 11973 (2017)
- [3] A. Porter, *Chem* **5**, 2264 (2019)
- [4] T.C. Davis, *ACS Nano* **15**, 1426 (2021)
- [5] E.N. Lang, *ACS Nano* **15**, 10275 (2021)
- [6] A. Shi, *Angewandte Chemie* **60**, 25436 (2021)
- [7] A. Shi, *ACS Nano* **15**, 15429 (2021)
- [8] A. Shi, *ACS Applied Materials & Interfaces* **14**, 22634 (2022)
- [9] J.C. Arango, *ACS Applied Materials & Interfaces* *in press* (2022)

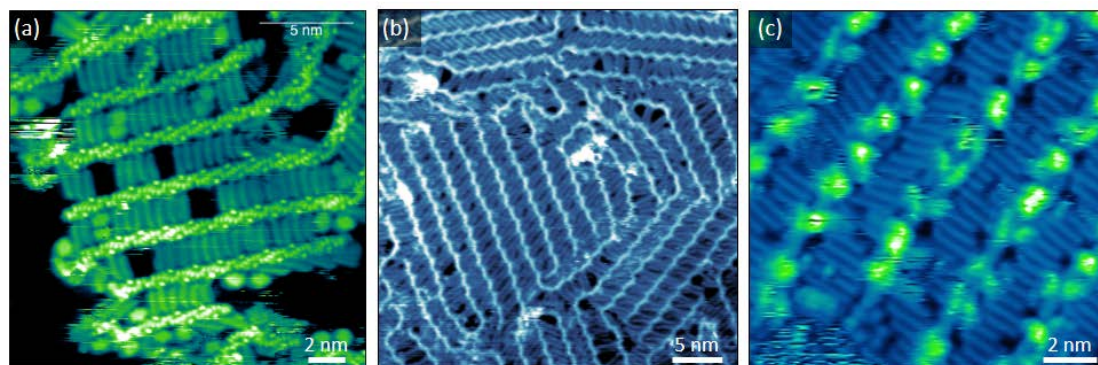
Primary and secondary structure of conjugated polymers uncovered by ESD-STM

G. Costantini¹

¹*School of Chemistry, University of Birmingham, Birmingham, UK*

In this talk I will demonstrate that ultrahigh vacuum scanning tunnelling microscopy (STM) is capable of delivering crucial information — that cannot be achieved by any other current analytical method — about “real world” electronic and energy materials. In particular, I will show that by combining vacuum electro spray deposition (ESD) and high-resolution STM, it is possible to image conjugated polymers used in organic electronics and photovoltaic devices with unprecedented details.

Based on this, it becomes possible to sequence the polymers by visual inspection and to determine their molecular mass distribution by simply counting the repeat units. Moreover, I will demonstrate that we can precisely determine the nature, locate the position, and ascertain the number of synthetic defects in the polymer backbone.¹⁻² The analysis of our high-resolution images univocally demonstrates that one of the main drivers for backbone conformation and polymer self-assembly is the maximization of their sidechain interdigitation. On this basis, we investigate the 2D assembly of a series of conjugated polymers with the aim of gaining insight in the molecular microstructure of the corresponding 3D functional thin films.^{4,5}



High-resolution STM image of (a) poly(C₁₄DPPF-F), (b) pBTTT, and (c) IDT-BT on Au(111).

References

- [1] D.A. Warr, *et al.*, *Sci. Adv.* **4**, eaas9543 (2018).
- [2] M. Xiao, *et al.*, *Adv. Mater.* **32**, 2000063 (2020).
- [3] H. Chen, *et al.* *J. Am. Chem. Soc.* **141**, 18806 (2019).
- [4] R.K. Hallani, *et al.*, *J. Am. Chem. Soc.* **143**, 11007 (2021).

Formation and functionalization of 2D materials: a molecular approach

S. De Feyter¹

¹*KU Leuven, Leuven, Belgium*

In this presentation, I will mainly focus on the functionalization of graphite, graphene, and transition metal dichalcogenides using molecules, though the concepts can be applied to other 2D materials too. Nanostructuring is at the heart of all functionalization protocols that we develop because it opens new possibilities for control and functionality. A variety of scanning probe microscopy methods are used for visualization, characterization, and manipulation. The first approach is based on molecular self-assembly at the interface between a liquid or air, and graphite or graphene. A second approach is based on the covalent attachment of molecules on 2D materials via covalent chemistry. It will be demonstrated how in addition to bottom-up strategies that provide control on the density and layer thickness, as well as submicron to nanoscale nanostructuring, also top-down scanning probe microscopy and optical lithography can be used to structure such covalently modified surfaces. A third approach does not focus on the functionalization of the surface, but uses the surface as a support for the in-plane covalent stitching of molecules, leading to the formation of on-surface 2D dynamic covalent polymers.

References

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- [4] M. C. Rodríguez González, A. Leonhardt, H. Stadler, S. Eyley, W. Thielemans, S. De Gendt, K. S. Mali, S. De Feyter, *ACS Nano* **6**, 10618 (2021)
- [5] S. Freddi, M. C. Rodriguez Gonzalez, P. Carro, L. Sangaletti, S. De Feyter, *Angew. Chem. Int. Ed.* **61**, e202200115 (2022)
- [6] G. Zhan, Z.-F. Cai, M. Martínez-Abadía, A. Mateo-Alonso, S. De Feyter, *J. Am. Chem. Soc.* **13**, 5964 (2020)
- [7] G. Zhan, Z. F. Cai, K. Strutyński, L. Yu, N. Herrmann, M. Martinez-Abadia, M. Melle-Franco, A. Mateo-Alonso, S. De Feyter, *Nature* **603**, 835 (2022)

Two Dimensional Polymers and Polymerizations

Austin M. Evans,¹ Ioannina Castano,¹ Xavier Aguilar-Enriquez,¹
Rebecca L. Li,¹ Anton D. Chavez,¹ Anusree Natraj,¹ Woojung Ji,¹
Michael J. Strauss,¹ and William R. Dichtel¹

¹Department of Chemistry, Northwestern University, Evanston IL 60208 USA

Abstract: Synthetic chemists have developed robust methods to synthesize discrete molecules, linear and branched polymers, and disordered cross-linked networks. However, two-dimensional (2D) polymers prepared from designed monomers have been long missing from these capabilities, both as objects of chemical synthesis and in nature.¹ Recently, new polymerization strategies and characterization methods have enabled the unambiguous realization of 2D, covalently linked macromolecular sheets. In the early realization of this synthetic challenge, polymerization conditions were identified empirically by screening polymerization conditions through powder x-ray diffraction analysis of the insoluble powder products, which provided polycrystalline samples with crystalline domains with average in-plane dimensions of 25-50 nm. More recently, we have developed tools to study these polymerizations experimentally^{2,3} and computationally, which has given rise to the first controlled two-dimensional polymerizations, along with materials of improved quality (Figure). I will present these approaches and the properties of high-quality 2D polymers that are now starting to emerge.

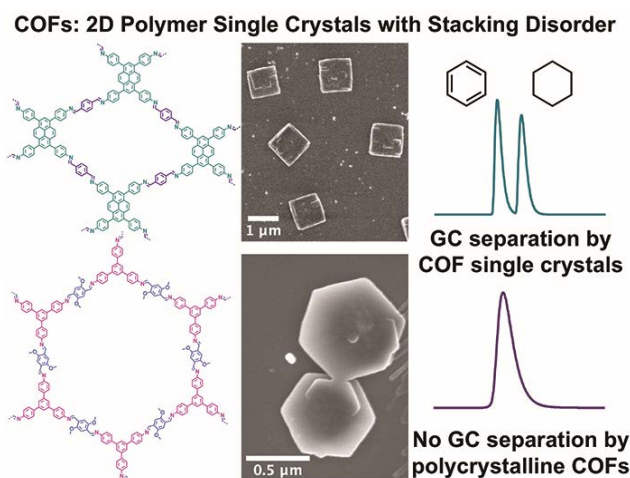


Figure. Micron-scale single crystals of imine-linked 2D covalent organic frameworks and chromatograms indicating their ability to separate benzene and cyclohexane.

References

- [1] Evans, A. M. *et al.*, *Chem. Rev.* **122**, 442-564 (2022)
- [2] Evans, A. M. *et al.*, *Science* **361**, 52 (2018)
- [3] Natraj, A. *et al.* *J. Am. Chem. Soc.* Accepted. (2022)

Towards Understanding and Controlling On-Surface Coupling Reactions and Self-Assembly Mechanisms

Daniel Ebeling^{1,2}

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²*Center for Materials Research, Justus Liebig University Giessen, Giessen, Germany*

Constructing organic nanomaterials with tailored size and connectivity is challenging yet often the key for applications in molecular electronics since the (opto-)electronic properties of the quantum materials are highly structure dependent. Our goal is to develop new strategies for synthesizing such organic materials on surfaces. Therefore, in-depth knowledge about the molecular self-assembly and reaction mechanisms is needed, which we can obtain via the atomic force microscopy (AFM) bond imaging technique. Recently, we could demonstrate that the surface may act as a control knob for tuning the self-assembly process of organic compounds via reversing the binding selectivity of intermolecular halogen bonds. [1] In another study, we used the AFM tip for building covalent nanostructures one molecule at a time on an inert sodium chloride surface, while tracking the structural changes with single-bond resolution (Figure 1). Covalent homo-dimers in *cis* and *trans* configurations and homo-/hetero-trimers were selectively synthesized by a sequence of dehalogenation, translational/rotational manipulation and intermolecular coupling of halogenated precursors. In addition, complex bonding motifs such as a carbon–iodine–carbon bond and fused carbon pentagons were created. This approach enables synthesizing elusive covalent nanoarchitectures, studying structural modifications and revealing pathways of intermolecular reactions. [2]

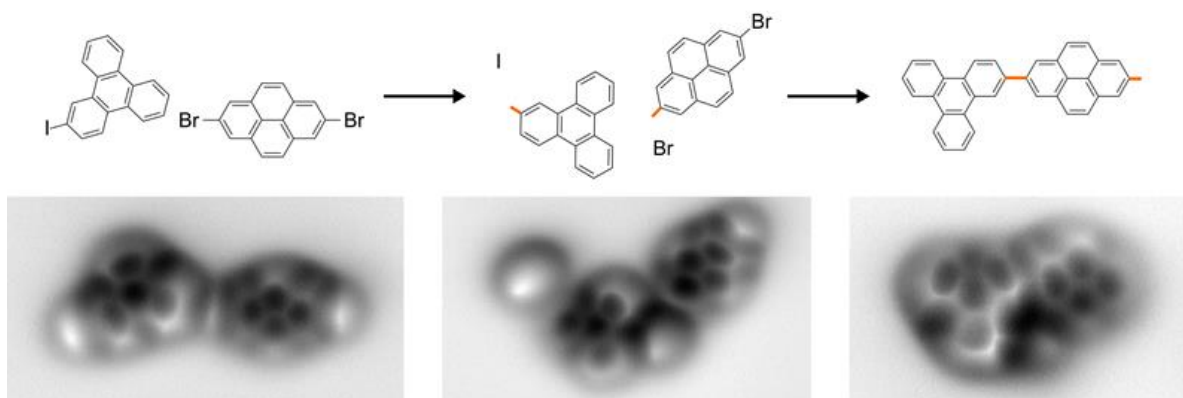


Figure 1: Constructing organic nanoarchitectures by scanning probe manipulation. First, the precursors are activated by local voltage pulses. Subsequently, the formed radicals are moved together with the AFM tip. Finally, a covalent carbon–carbon bond is formed via another voltage pulse.

References

- [1] J. Tschakert et al. *Nature Communications* **11**, 5630 (2020)
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On-surface synthesis of π -conjugated polymers

D. Écija¹

¹ IMDEA Nanoscience, Madrid, Spain

On-surface synthesis has emerged as a powerful strategy to design unprecedented nanomaterials. In this talk, I will revise our recent achievements regarding the synthesis of one-dimensional π -conjugated polymers, featuring emerging physical properties such as non-trivial topology or π -based magnetism.¹⁻⁶



References

- [1] Advanced Materials **33**, 2170349 (2021)
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Molecular Motion at Surfaces

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Molecular motion at surface is of interest for a better understanding of fundamental physical and chemical processes as molecular adsorption, interatomic interactions, atomic-scale friction or energy dissipation. In this talk, several studies of molecular motion at well-defined single-crystal surfaces will be presented, all using scanning tunneling microscopy (STM) to characterize molecules moving on surfaces.

Molecular motion is induced by various stimuli as heat and light [1], chemical interaction with the STM tip [2-4], electric current or electric fields in the STM junction [5-7]. Metallic single-crystal surfaces with a highly defined lattice and corrugation are used as substrates. Experiments under

ultrahigh vacuum and mostly at low temperatures of 5K allow to follow the motion of single molecules with time. Key challenges in these studies are to

- control the molecular motion in terms of direction and precision
- achieve unidirectional motion against the principle of microscopic reversibility
- investigate how far and how fast single molecules move

Various examples, including recent results, from our research group will be discussed along these main points.

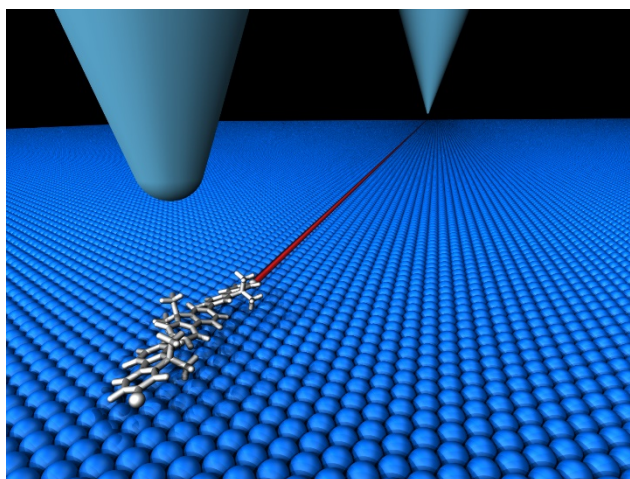


Figure: Schematic view of a single molecule being transferred between two STM tips [7].

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On-surface synthesis and SPM characterization of polyradical PAHs with strong multireference character

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The recent progress in on-surface synthesis enabled to form new molecular structures, which are not available by traditional organic chemistry in solution [1]. Special attention was paid synthesis of open shell polyaromatic hydrocarbons (PAH) showing interesting magnetic properties [2]. So called π -magnetism in PAHs is introduced by either by frustrated topology of bipartite lattice or by electron-electron correlation [3]. The most of the PAH molecules prepared so far had a biradical character, where the description of the electronic structure can be well understood using the single determinant mean field methods such as DFT. Recently, few examples of polyradical molecules with multireference character has been reported [4].

In this talk, we will present synthesis of polyradical molecules with strong multireference character. Their electronic structure is analyzed using SPM technique including nickelocene functionalized probes as well as DMRG and CAS calculations which enables to describe properly the multireference states. First, we will discuss a triangulene-based molecule, where tetradical character is introduced in combination of the e-e interaction as well as the frustrated topology. We will also discuss the effect of the pentagon defects on the electronic structure as well as coexistence of Kondo and spin excitation in defective molecules. In second part, we will describe polyradical PAH macrocycles with eight-to-ten unpaired electrons. This cyclic system features frustrated magnetism with a strong entanglement between unpaired spins. Therefore, it represents an example of spin liquid hosted in a single molecule.

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Structural Transitions of Molecules on Surfaces

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Molecules on surfaces offer an impressive variability for creating functional structures at surfaces. Metal-carrying molecules constitute a particular interesting example as they allow for creating an ordered array of metal atoms on a surface. To exploit the full potential of such metal arrays, however, the support surface should be electrically insulating. On many insulator surfaces, however, controlled molecular structure formation is hampered by the weak molecule-surface interaction. In a recent work, we have electrostatically anchored dimolybdenum tetraacetate (MoMo) molecules onto calcite (10.4) at room temperature [1]. In this system, the molecules act as hard spheres that adopt well-defined adsorption positions, resulting in a regular array of metal atoms on this bulk insulator surface.

On the (111) surface of copper, the MoMo molecules are shown to undergo a reversible phase transition of molecular islands (2D solid phase) into mobile molecules (2D gas phase). Interestingly, while this phase transition is usually associated with heating, the mobilization of the MoMo molecules presented here is observed upon cooling [2]. In this talk, the molecular-scale origin of this inverse phase transition is discussed.

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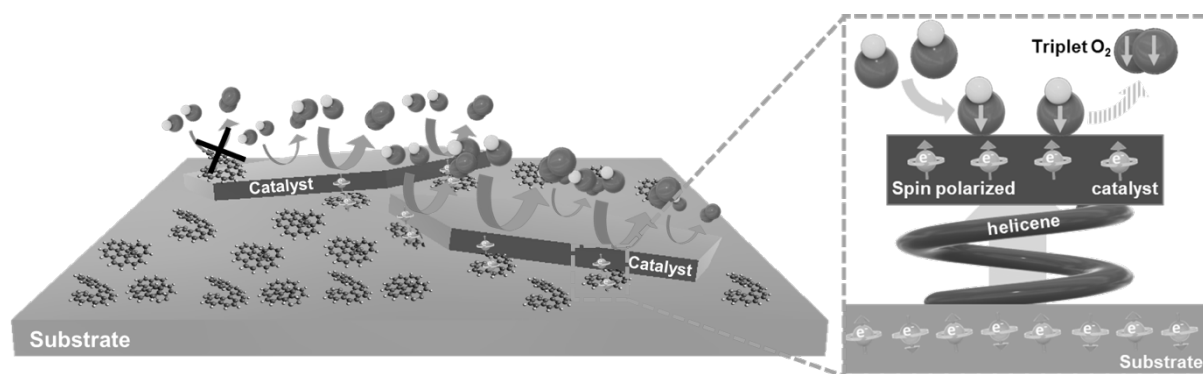
Hands up! Spin up! Chiral molecular layers controlling achiral electrocatalysis

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A sustainable future demands a successful transition from a carbon-energy dependent economy towards renewable energy schemes. The development of efficient catalysts, that could either convert chemical energy into electricity or use electrons to produce chemical energy, is a key milestone in our path to clean energy. In general, electrocatalysis studies focus on the interactions (e.g., electron transfer) between the catalyst surface and the reaction intermediates. However, the role of electron spin, as an intrinsic property of electrons, has commonly been overlooked.

In this talk, I will show you how using chiral self-assembled monolayers we can enhance and tune the activity and product selectivity at state-of-the-art 2D catalysts via spin-polarization mechanisms and chiral-induced spin selectivity (CISS) effects [1-2].



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Molybdenum Disulfide on Au(111) – growth, electronic structure and versatile playground for single molecule spectroscopy

**Christian Lotze, Nils Krane, Gaël Reecht, Nils Bogdanoff
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Scanning tunneling spectroscopy (STS) is a tool that allows to address individual molecules in a precisely known surrounding. However, it bears the drawback that it requires a conductive substrate. Deposition of organic molecules on a metal substrate leads to strong hybridization of the electronic states. Preservation of the molecular character requires the inclusion of thin band-gapped materials.

In my presentation I will show that, and why, MoS₂ can act as an effective electronic decoupling layer that exhibits also a small electron-phonon coupling strength. Differential conductance spectra of 2,5-bis(3-dodecylthiophen-2-yl)thieno[3,2-b]thiophene (BTTT) molecules exhibit a multitude of sharp characteristic peaks, originating from vibronic states. These vibronic fingerprints of different molecules allow for an identification of different rotamers. DFT calculations of the molecules in gas phase provide all details for an accurate simulation of the vibronic spectra of both investigated rotamers [1].

Moreover, we will make use of the vibronic fingerprints to investigate the influence of the tip potential on the apparently shifted molecular states along the extended molecular backbone of BTTT [2]. Finally, the impact of molecular vibrations on spatial variations of the molecular conductance on BTTT and H₂Pc will be discussed and will allow us to understand a vibrational excitation mechanism in tunneling spectroscopy beyond the Franck-Condon model [3].

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Dynamic charge-transfer at functional metal-organic interfaces: What is it and how can we control it?

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When organic molecules are in contact with metallic surfaces, localized molecular electronic levels couple with a continuum of electrons in the metal. This can potentially yield charge rearrangements at the interface. This effect is of great relevance during the formation of organic-metallic thin-films, during molecular gas-surface reactions, and when manipulating single molecules at surfaces. The specific level alignment is sensitive to dynamic molecular motion and to changes in the electronic structure, be they thermal or non-thermally driven by external stimuli. First principles calculations can help us to reveal the effects of charge transfer on the structure, the electronic properties and the spectroscopic signatures of metal-organic interfaces. [1] In this talk, I will show how state-of-the-art electronic structure theory, core-level spectroscopy simulations and molecular dynamics simulations at surfaces provide insights into the taxonomy of static and dynamic charge-transfer scenarios at interfaces, how these scenarios contribute to measurable properties, and how we can exert control over charge transfer. I will cover examples ranging from self-assembled two-dimensional donor-acceptor networks [2], topological defects in graphene, [3] single molecule manipulation, [4] to molecular beam scattering [5].

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Polymeric wires, nanoribbons and 2d-molecular networks studied by scanning probe microscopy

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On-surface chemistry is used to assemble polymeric wires [1], nanoribbons [2] as well as 2d-molecular networks [3]. Pulling of wires and ribbons is used to investigate the lateral motion as well the detachment of individual sub-units. The motion of graphene nanoribbons shows evidence of superlubricity. Sequential bending and twisting around single C-C bonds is observed in the case of poly-pyrenylene chains. 2d-molecular networks have promising electrical and magnetic properties as indicated by the formation of flat bands. In the case of the assembly of tetrabromo-1,3,6,8 tetraazapyrene (TBTAP) on Pb(111), neighboring rows of radicals and neutral molecules are observed [4]. Charged molecules host spin $\frac{1}{2}$ electrons, which is confirmed by high resolution dl/dV spectroscopy, where Yu-Shiba-Rusinov (YSR) states in the superconductive gap are observed. At edges of the molecular islands zero bias peaks are observed, which indicates the existence of Majorana bound states. Discharging of molecules is found by the application of positive voltages, where the formation of Coulomb blockade rings is observed.

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Dual Functionality of Single Molecule Machines: Rotors and Nanocars

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Controlling rotations and translations at the single molecule level represents a fascinating scientific goal, which can be now reached for selected compounds under the tip of a scanning tunneling microscope (STM) [1]. Recent examples were provided by Nanocar Race II, which was not only a successful dissemination event, but also a unique long-time experiment on the parallel manipulation of eight nanocars by voltage pulses [2]. However, the rational design of single-molecule machines still requires a deeper understanding of the physical mechanisms inducing controlled movements on a surface.

Tunneling electrons originated from the STM tip can inelastically excite specific conformational or vibrational molecular degrees of freedom, producing controlled rotations or translations. On the other hand, the thermal excitation of the substrate also induces movements in adsorbed molecules, showing that some molecular degrees of freedom can be addressed also thermally [3]. Even if the excitation mechanisms for rotors and nanocars are probably similar, rotation requires a strong local molecule-substrate interaction providing a rotational axle, while a nanocar moves fast if its adsorption is weak. It is therefore unusual that the same species presents both functionalities.

In this talk, we will focus on the investigation of P-DMBI-based zwitterionic molecules. Thanks to its internal charge separation and the possibility to both chemisorb and physisorb on the Au(111) surface, this class of molecules represents an ideal model system to study inelastic tunneling electrons based manipulation, allowing the comparison of unidirectional rotations and translations on the same compound. Furthermore, combining long-time electronic excitations with the slow controlled increasing of the substrate temperature we could observe rare rotational events and compare the role of inelastic tunneling electrons and thermal excitations in the controlled rotation of the single-molecules.

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Magnetism in Engineered Graphene Nanostructures

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Graphene is inherently a non-magnetic material and lacks spin-orbit coupling. However, graphene nanostructures can spontaneously develop intrinsic paramagnetism due to the stabilization of open shell configurations in its electronic structure. Radical states of a conjugated graphene lattice, as singly occupied states, respond to the presence of finite Coulomb correlations by localizing electrons with a net spin polarization. In this presentation, I will show recent results on spin-hosting nanographenes, including their synthesis routes on a metallic substrate [1], methods for detecting their magnetic fingerprints, and the origin of such unconventional form of magnetism. We use scanning tunneling microscopy and spectroscopy to detect and spatially localize the spin density by mapping the amplitude of a Kondo resonance [2,3,4,6] or spin excitations [2,5]. Among the studied systems that will be presented here, I include a family of triangulenes with varying size [5,6], chiral graphene nanoribbons [7] and ribbons doped with boron heteroatoms [2,8].

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Accessing non-equilibrium states at atomic scales

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Scanning probe microscopy (SPM) has revolutionized our understanding of the atomistic world. Conventional SPM, however, is an inherently slow technique – too slow to capture transition states in excitation processes in most cases. While ultra-fast non-equilibrium phenomena is enabled by terahertz (THz) scanning tunneling microscopy (STM) [1], another approach gives us access to intermediate timescales that are relevant for spin precession and relaxations. We introduce a novel variant of SPM by combining principles of STM and atomic force microscopy (AFM). Instead of the usual direct current in conventional STM, we drive a tiny alternating current between the microscope's tip and a single molecule under study. We exploit the single-electron sensitivity of AFM [2] in detecting the current which consists of only a single electron per AFM-cantilever oscillation cycle, tunneling back and forth between tip and molecule. This enables operation in absence of any conductance of the underlying substrate, while retaining the capability of imaging electronic states with sub-angstrom resolution. Thereby, we can access out-of-equilibrium charge states that are out of reach for conventional STM [3]. Combined with electronic pump-probe spectroscopy [4], this enables the direct measurement of the triplet lifetime of an individual molecule, for example. The combined resolution in space and time in this case offers previously unexplored routes to control and study local spin-spin interactions [5].

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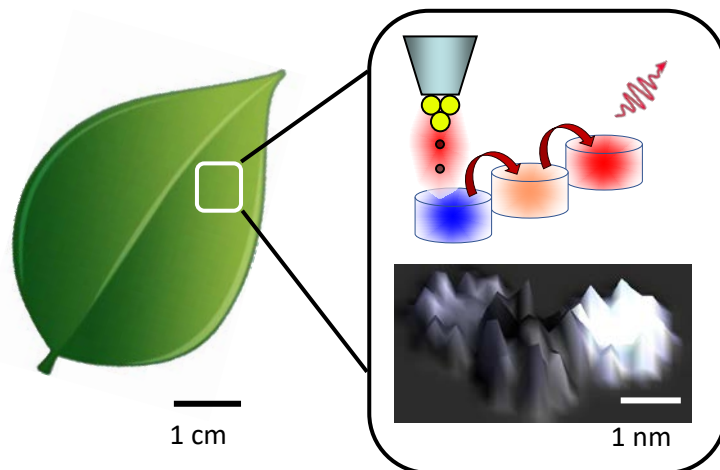
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Hyper-resolved fluorescence microscopy of molecular and extend systems.

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The electric current traversing the junction of a scanning tunneling microscope (STM) can be used to generate sub-molecularly resolved fluorescence maps of individual molecules decoupled from a metallic substrate by a thin insulating NaCl layer. Combined with spectral selection and time-correlated measurements, this hyper-resolved fluorescence microscopy approach [1] allowed us to scrutinize the vibronic structure of individual molecules [2] in a very similar way than in the recent TERS reports, without requiring an optical excitation. We used this approach to characterize the photonics properties of charged species [3] to track the motion of hydrogen atoms within free-based phthalocyanine molecules [4], and to address exciton diffusion between complex chromophore architectures [5], graphene nanoribbons [6], or 2D semiconductors [7].



Probing energy transfer in model molecular systems with STM

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Control of charge transfer into organic molecules on surfaces

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Charge transfer processes through ultrathin, supported oxide films have received increasing attention in recent years because of the possibility to control the charge state of adsorbates or the direction of catalytic reactions. The main driving force for the occurrence of charge transfer in these systems is the reduction of the substrate work function induced by deposition of the oxide film in combination with an adsorbate of relatively high electron affinity. While previous studies have focused on the charging of metal atoms or small molecules, we have recently extended these investigations to charge transfer processes into organic molecules. In this contribution, we present results on the adsorption and charging of model organic semiconductors (e.g. pentacene (5A), 2H-porphine (2H-P), 2H-tetraphenylporphyrin (2H-TPP) and others) on ultrathin MgO(001) films supported on Ag(001). By combining scanning tunneling microscopy and photoemission spectroscopy and tomography, we identify and quantify charge transfer into the organic monolayer film. In addition, we show that by tuning the work function and/or the MgO thickness it is possible to control: the ratio of charged and neutral species, the number of electrons transferred and, concomitantly, the conformation of the adsorbates.

Supramolecular Self-assembly and Metal-Ligand Redox Assembly at Surfaces

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The central theme of materials chemistry is the dependence of function on structure with the challenge to design composition and structure to achieve novel function. In molecular materials, the selection and positioning of specific functional groups will direct packing and stacking, which determine the electronic and chemical properties of molecular thin films and semiconductors. Design of molecular ligands for metal-organic complexation at surfaces can address the long-standing grand challenge of high selectivity in heterogeneous catalysis. Our group is working to develop principles of on-surface molecular self-assembly¹ and of metal-organic complexation² to gain new insight into molecular layers and new chemical activity at metal single-site catalysts.³ This work involves close collaboration with multiple research groups to synergistically combine talent in design, synthesis, sample preparation, characterization, analysis, theory, and computational modeling. Our group uses a range of surface characterization tools to interrogate these systems under well-controlled environments, including scanning probe microscopy, photoelectron spectroscopy, vibrational spectroscopy, and mass spectrometry. We investigate systems under a variety of conditions: solution/solid interface, ultra-high vacuum, and flow reactor conditions at high temperature and high pressure. Here, I will report on recent results in several aspects of this work. We have demonstrated the impact of conformational entropy in impeding self-assembly, but that this can be overcome with appropriate selection of co-solutes. Metal-organic complexes at surfaces can be designed to achieve single-site metal centers in which we can observe redox isomerism, control of metal oxidation state, transmetallation, and chemical spillover to the support. We have transferred this design concept for single-site catalysts to high-surface-area powder oxide supports and shown that these can operate as effective catalysts in solution and under gas flow conditions. Ongoing work will seek to extend understanding of these systems to achieve molecular thin films and single-site catalysts of greater complexity.

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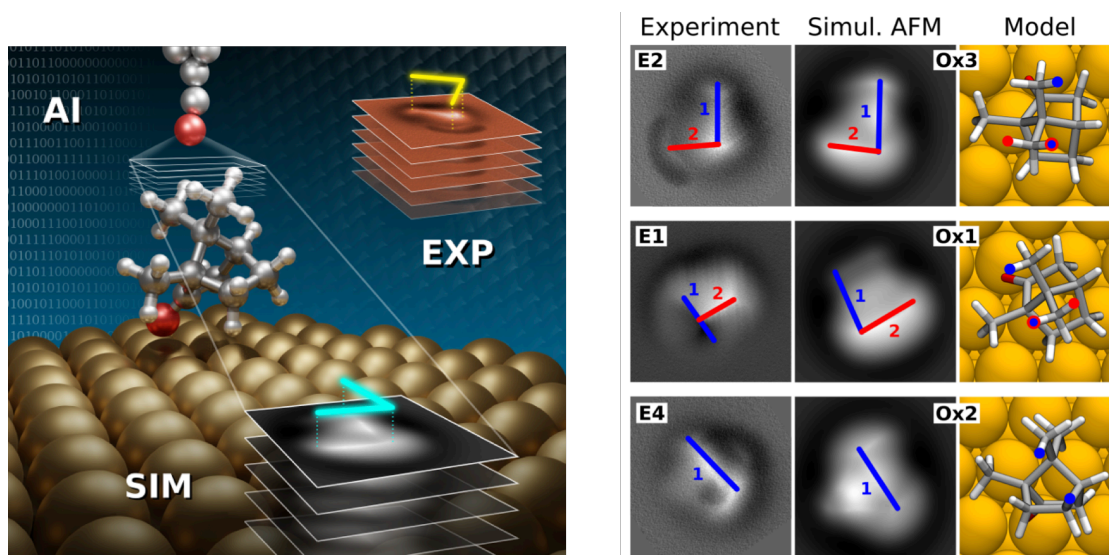
Bayesian Inference of Surface Adsorbates

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Adsorption of molecules on surfaces and their electronic contact are important parameters in controlling the mechanisms of catalysis, sensing, or optoelectronics. Powerful tools like atomic force microscopy (AFM) can resolve many conjugated adsorbates, but not full adsorption configurations, active sites or non-planar molecules. Density-functional theory (DFT) simulations are widely used to simulate and characterise organic adsorbates. These studies require a preliminary adsorption structure search, a complex procedure is often approximated by experimental estimates or chemical intuition. We combine active learning techniques with DFT to accelerate structure search at organic/inorganic interfaces, free of human bias.

In the Bayesian Optimization Structure Search (BOSS) [1], we fit surrogate models of the adsorption energy landscape to DFT data, then refine the landscape by smart sampling of further configurations. In a BOSS study of (1S)-camphor adsorbing to the Cu(111) surface, we identified 8 unique stable adsorbates and demonstrated that both chemisorption and physisorption can take place [2]. These findings shed light on non-contact AFM images, where different orientations of this bulky molecules were experimentally observed but the data was inconclusive. We compared simulated and experimental AFM images to establish the exact configurations behind the images and study their electronic properties [3]. This study demonstrates the power of new cross-disciplinary tools in detecting complex interface structures.



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In-situ ToF-SIMS as a tool to study on-surface synthesis: unraveling the fates of atomic hydrogen

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In this talk, the application of time-of-flight secondary ion mass spectrometry (ToF-SIMS) as a tool to study chemical reactions at surfaces is discussed. The advantages, unique capabilities, disadvantages and limits of this approach are discussed. It is shown that in-situ ToF-SIMS is formidable tool to explore C-C coupling reactions and hydrogenation/dehydrogenation chemistry in large molecules up to ~4000 u.

With focus on hydrogen at surfaces and in combination with other surface analytical tools, the kinetics of atomic H in the desorption of Br as HBr in consequence to forming a C-C bond formation by cyclodehydrogenation is deciphered.^[1,2] It is also shown that atomic H cleaves C-C bonds in geodesic polycyclic aromatic hydrocarbons.^[3] Finally, by H/D isotope exchange the dynamic nature of hydrogen in polycyclic aromatic hydrocarbons (PAHs) at hot metal surfaces is demonstrated.^[4]

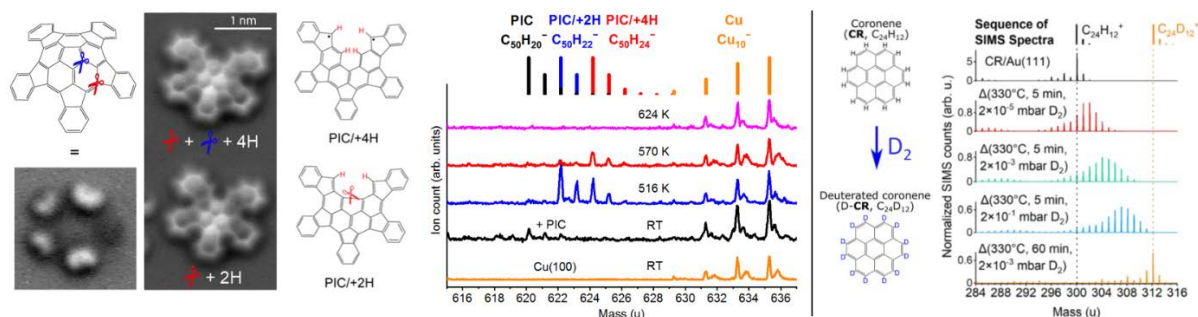


Figure 1: (Left) Hydrogenation and C-C bond cleavage in pentaindenocorannulene on Cu(100) studied by non-contact atomic force microscopy and ToF-SIMS. (Right) H/D isotope exchange in coronene on Au(111) revealed by ToF-SIMS.

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Chiral Nanostructures Constructed *via* On-Surface Chemistry

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Chirality continues to be research hotspot due to its potential applications in asymmetric catalysis, nonlinear optics, pharmacy, etc. In recent decades, the emerging on-surface chemistry has provided an unprecedented route towards the building of two-dimensional (2D) chiral nanostructures. The representative feature for 2D chirality is that achiral and prochiral tectons are likely to produce chiral nanostructures. The 2D chiral nanostructures can be either noncovalent or covalent. The noncovalent chiral systems could find applications in fields like chiral separation, whose investigations facilitate the understanding of chiral phenomena including resolution, transfer and amplification. The covalent chiral structures exhibit excellent thermal and chemical stability, whose formation process offers crucial guidance for homochiral and heterochiral intermolecular coupling reactions. With the aid of scanning probe microscopy, both types of nanostructures can be identified at submolecular scale.

In this presentation, we will report our recent studies of 2D chiral nanostructures built *via* on-surface chemistry method. The chiral structures and formation mechanisms were monitored and elucidated by combined scanning tunneling microscopy (STM), synchrotron radiation photoemission spectroscopy (SRPES), and density functional theory (DFT) calculations. The topic includes: (1) Noncovalent chiral nanostructures generated by depositing hydroxyl-terminated molecules [1] and terminal alkynyl bromides [2] on Ag(100), and (2) Covalent chiral nanostructures produced by prochiral terminal alkynes undergoing Bergman cyclization reaction followed by heterochiral cross-coupling on Ag(111) [3], and the intermolecular reactions of a prochiral organohalide on Ag(111). [4]

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Abstracts of Posters

(in alphabetical order)

Microscopic Insight in the structure of an Ionic Liquid [C₁C₁Im][Tf₂N] on Cu(111): An Integrated Experimental and Theoretical Investigation

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We studied the adsorption and reaction behavior of the ionic liquid (IL) 1,3-dimethylimidazolium bis[(trifluoromethyl)sulfonyl]imide ([C₁C₁Im][Tf₂N]) on Cu(111) using non-contact atomic force microscopy (nc-AFM), scanning tunneling microscopy (STM), and angle-resolved X-ray photoelectron spectroscopy in ultrahigh vacuum (UHV) as a function of temperature, supported by density functional theory (DFT) calculations. Our AFM results show that at 200 K the ILs self-assemble into a highly ordered structure, with cations and anions arranged next to each other in a checkerboard-type phase. After extended annealing at 300 K, the structure transforms to a porous honeycomb-type phase, and finally at 350 K to a disordered amorphous phase. Complementary XPS shows no IL desorption until 300 K; however, all anions-related peaks show pronounced shifts to lower binding energy, indicative of a chemical transformation, while the cation-peaks remain unchanged. Upon heating to 360 K, ~50% of anions or their fragments desorb from the surface.

Chemical sensing with CN-functionalized chiral graphene nanoribbons

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N. Sumi³, J. Castro-Esteban⁴, J. Lawrence², J. Li⁵, P.
Brandimarte¹, D. S. Portal^{1,2}, F. Schiller^{1,2}, L. Schio⁶, L. Floreano⁶, D.
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High levels of pollution have made accurate environmental monitoring an increasing priority. A solution to the current demands of sensing technologies are solid-state gas sensors incorporating custom-made materials. However, such devices lack selectivity. One potential application for graphene nanoribbons (GNR) is their implementation in electronic and sensing devices, thanks to edge functionalization and metal coordination. Monitoring the changes in the electronic structure of the GNRs when small gas molecules interact with functionalized GNRs may be a way to realize selective detection of gases. In this context chiral graphene nanoribbons (chGNRs) with electron-withdrawing cyano (CN) edge groups are studied.

In this work we first explore the electronic structure of CN-chGNRs and CN-chGNRs coordinated to Fe or Co atoms by means of scanning tunneling microscopy and spectroscopy (STM / STS) and angle resolved photoemission spectroscopy (ARPES). Whereas the band gap of CN-chGNR (990 mV) is larger than that of pristine chGNR (700 mV), it shrinks to only 500 mV upon metal-coordination.

Then we study the influence of O₂ and NO₂ exposure on the electronic properties of these GNRs, using STS, X-ray photoelectron spectroscopy (XPS) and near edge X-ray absorption fine structure spectroscopy (NEXAFS). Previous studies show pristine chGNRs are easy to react with O₂ and H₂O, which makes them unsuitable for gas sensing applications. In contrast, no obvious changes were observed after O₂ dosing onto CN-chGNR and metal-coordinated CN-chGNR. However, metal-coordinated CN-chGNR show notable sensitivity to NO₂. Our results go one step further into the understanding of the interaction mechanism at the atomic level between CN-chGNRs and gases as sensor-analyte devices.

A highly drift stable low temperature STM based on a flow cryostat

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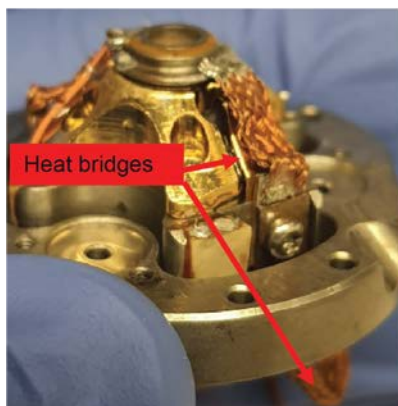
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Scanning-Probe-Microscopy is the prevalent tool to characterize structural and electronic properties of organic nanostructures on surfaces. Additionally, electronic properties can be measured locally with a high spatial resolution with scanning tunneling spectroscopy (STS). For Scanning-Tunneling-Microscopy, delicate molecular systems require very low imaging currents and low drift is always an asset. The aim here is to further develop an existing low-temperature STM based on a flow cryostat to facilitate STS also at liquid nitrogen temperatures.

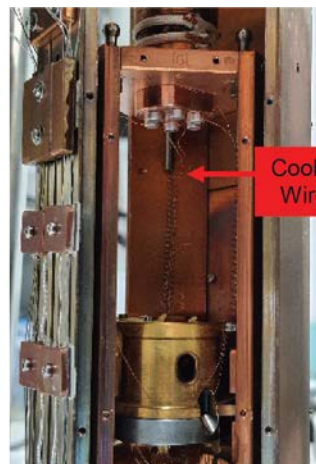
To minimize thermal drift, we optimized the heat flow to and within the core STM by several measures:

- careful thermal anchoring of control and signal wires. Thereby, using an uninterrupted signal wire facilitates imaging with setpoint currents in the low pA range
- avoiding materials with a low heat conductivity by design whenever possible
- introducing heat bridges and additional cooling wires to optimize the heat flow in order to promote thermal equilibration
- using quartz-glass windows or shutters to avoid heat uptake by IR stray radiation from the surrounding

These combined measures resulted in an exceedingly high temperature stability of the STM with temperature variations < 10 mK. Thereby, the STM became highly drift stable even at ~ 80 K using a flow cryostat. This is demonstrated by deactivating the feedback for several minutes with current changes remaining $< 5\%$.



(a)



(b)



(c)

(a) STM scanner head with copper heat bridges (b) STM housing with additional cooling wires connecting the STM and cryostat cold head (c) quartz-glass windows to avoid IR radiation.

Bias-dependent switching of molecular nanostructures at the solid-liquid interface: the influence of concentration

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Research into the switching between different molecular phases at the solid-liquid interface induced by external triggers has gained increasing attention in the past years. For example, the switching induced by an external electric field has been achieved for carboxyl-functionalized molecules at the liquid-HOPG interface. However, different mechanisms for the switching are still discussed¹⁻³. Here we discuss the influence of concentration on the bias-dependent switching of a triarylamine derivative at the nonanoic acid-HOPG interface studied by scanning tunneling microscopy. For a fully saturated solution, a porous phase (chicken-wire) was observed for negative sample bias and a close-packed phase was observed for positive sample bias. For a 50% saturated solution, a second porous phase (flower) coexisted with the chicken-wire phase at negative sample bias, while the close-packed phase was observed at positive sample bias. For a 20% saturated solution, both porous phases and the close-packed phase coexisted at positive sample bias, while the two porous phases were observed at negative bias. For all concentrations investigated, switching between the porous phases and close-packed phase was accomplished by changing the bias polarity. Additionally, the switching for a 10:1 mixture of the triarylamine derivatives and 1,3,5-tris(4-carboxyphenyl) benzene molecules at the nonanoic acid-HOPG interface was studied. The aim was to identify whether intermixed structures are formed and if the two molecules will influence each other's switching behavior. The results showed that no intermixed structures were formed. Instead, both molecules formed networks separately. The switching could still be initiated while it occurred for each molecule separately and no effect of cooperativity was detected.

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Conservation of Nickel Ion Single-Active Site Character in a Bottom-Up Constructed π -Conjugated Molecular Network

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The on-surface chemistry of metalloporphyrins is paramount for building functional devices precise at the molecular scale.^[1] The tailorable performance of single-active sites that are stabilized within their moiety introduces the unique opportunity to rationally design catalytic materials and chemical sensors as well as miniaturized spintronic devices.^[2–4] The technological exploitation of molecule-based materials relies on more robust covalent nanostructures.^[5,6] On-surface synthesis is the method of choice in order to achieve π -conjugated conductive nanomeshes with red-shifted absorption characteristics at the interface.^[7–9] Approaches combining local insights with space-averaging techniques were either limited to porphyrin materials without transition metal chelation or did not include the functional properties of the ligated cores that are provided by covalent metalloporphyrin networks. This gap is filled here by providing joint findings obtained by photoemission and absorption spectroscopy as well as scanning tunneling microscopy experiments. We have chosen Au(111) as the catalyst to induce Ullmann coupling of nickel tetra(4-bromophenyl)porphyrin.^[10] The creation of a π -delocalized porphyrin network across the surface is reflected by the appearance of continuous energy-dispersive electronic valence states. Concomitantly, the single-active site character of the Ni cores embedded in the conductive molecular backbone is retained.

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Role of Adatoms for the Adsorption of F4TCNQ on Au(111)

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The incorporation of native substrate adatoms within adsorbed molecular layers can significantly change the electronic structure at metal-organic interfaces. Consequently, the presence of adatoms within a molecular adlayer can affect the adsorption geometry, and bonding type of the adsorbed molecule as well as the work function of the interface.

Using density functional theory, we investigate the adsorption of F4TCNQ on Au (111)¹. We show that the Fermi-level pinning mechanism, and consequently, the charge transfer at the interface is significantly altered by the presence of adatoms within the molecular layer. Furthermore, we find that the adatom induces covalent coupling of the adsorbed molecules. Ultimately, the above-mentioned effects explain the energetic benefit of incorporating an adatom into the adlayer despite the energetic costs of extracting the adatoms.

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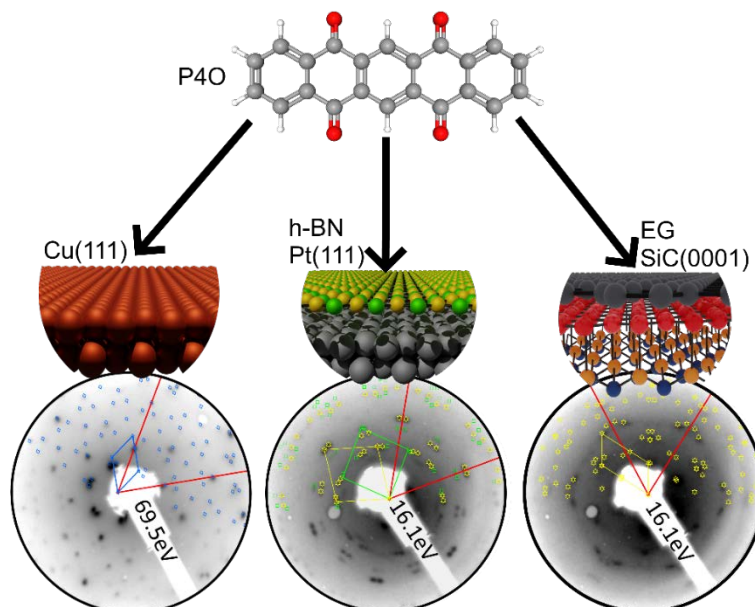
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Effects of oxygen functionalization on the molecule-substrate coupling

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5,7,12,14-Pentacenetetrone (P4O) is a polycyclic aromatic hydrocarbon (see figure) which shows promising electronic properties for batteries [1]. Unlike pentacene the π -system is not delocalized over the entire molecule. P4O shows a strong interaction with metal substrates up to a point where the π -system delocalization reemerges partially over the entire molecule [2]. To understand this phenomenon of metallic-organic bonding and charge-transfer, as well as the needed interaction strength for enabling a delocalized π -system over the entire molecule, different substrate – P4O systems have been investigated. On the one hand, Cu(111) has been chosen as a metallic substrate which shows a strong interaction and charge-transfer. On the other hand, the semi-metallic substrate of epitaxial graphene (EG) on SiC(0001) has been selected, showing no charge transfer. As an intermediate system, Pt(111) with a buffer layer of hexagonal boron nitride has been investigated. The change in the structure of the adsorbate film was analyzed using STM and LEED revealing a commensurate structure only for P4O on Cu(111). XPS and UPS measurements gain further insights into the electronic properties. Furthermore, photoemission orbital tomography (POT) has been used to characterize the energetic positions of the frontier orbitals.



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From open- to closed-shell character in molecular dimers of different coupling motifs

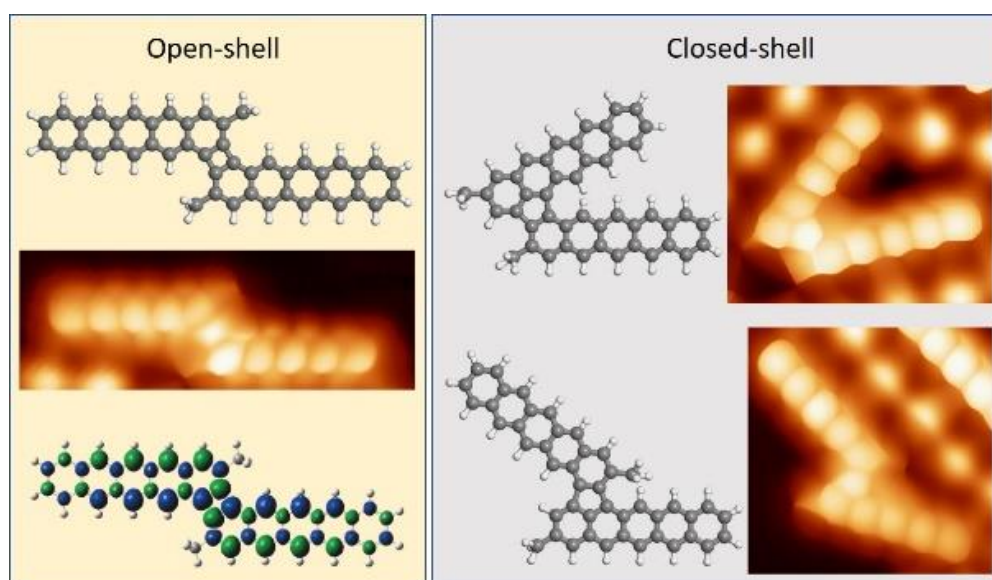
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On-surface synthesis (OSS) have rendered possible the characterization of π -magnetic carbon-based materials.¹ Building blocks, such as acenes, may be coupled covalently in order to build functional organic molecular materials of increasing size and complexity. Here, we report the OSS of pentacene dimers of differing coupling motifs on Au(111). Using scanning tunneling microscopy/spectroscopy and density functional theory, we characterized their electronic and magnetic properties. The various isomers reveal open-shell or closed-shell character, depending on the coupling motif. In particular, we demonstrate that the antiaromaticity of cyclobutadiene (as coupling motif) plays a decisive role towards the formation of open-shell structure. This illustrates how different coupling motifs may result in products of utterly different electronic properties; Understanding such structure-property relationships is necessary for designing such organic molecular materials.



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Tuning the chirality change of a single molecule by van der Waals interactions

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The chiral induction of molecules by non-covalent intermolecular interactions, like hydrogen bonding and van der Waals interactions, are crucial for understanding the fundamental mechanisms of chiral self-assembly [1] and heterogeneous asymmetric catalysis [2]. However, it remains challenging to address these subtle intermolecular interactions at the molecular level, especially the weakest of them, the van der Waals interactions. Here, we present a carbene molecule on a copper surface as a prototype of an anchored molecule with a facile chirality change upon excitation by inelastic electrons. A tiny change of the potential energy, introduced by weak van der Waals interactions with the tip of a scanning tunneling microscope, is sufficient to induce an asymmetric distribution of the two enantiomers of this molecule. Our findings reveal how an enantiomer is stabilized by van der Waals interactions at a single-molecular level, enabling an in-depth understanding of the elementary steps in chiral self-assembly and heterogeneous asymmetric catalysis.

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On-Surface assembly of graphyne-like networks on Ag(111) and Au(111)

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Graphyne is an sp-sp²-hybridized carbon allotrope with interesting electronic properties. However, the synthesis of monolayer graphyne flakes is elusive due to their high formation energy and high reactivity. Here, we report on the self-assembly and reaction of graphyne-like 2D networks built from 1,3,5-tribromo-2,4,6-triethynylbenzene (Br-TEB) molecules on Ag(111) and Au(111) using low-temperature scanning tunneling microscopy. Organometallic honeycomb networks are obtained upon debromination on Ag(111), while on Au(111), primarily covalent C-C bonds are formed. In addition, the poster discusses the effect of passivation groups and the position of the Br functionalization concerning the growth of graphyne-like 2D networks on metal surfaces.

Electric-field induced 2D polymerization/ depolymerization of boroxine-linked single-layer COFs at the solid/liquid interface

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Crystalline porous organic frameworks have drawn a lot of attention, given their applications in the devices of energy, gas storage, catalysis, separation, adsorption, and sensing. However, their characterization is challenging. Single-layer covalent organic frameworks (sCOFs), are single molecule thick, sheet-like macromolecules. sCOFs enable nanoscale characterization, which is one of the most important and challenging issues of the COF field in revealing structural insight into their function and properties.

On-surface synthesis of sCOFs is studied in our group, where a flattened and conductive surface is used as the 2D platform, and molecular-level characterization can be obtained by using scanning tunneling microscopy (STM). Beyond working as a visualization technique, STM also provides a highly localized, extremely strong, and switchable electric field (EF).

Our group showed control of the reversible phase conversion between self-assembled molecular networks (SAMNs) and covalent organic frameworks (COFs) by changing the orientation of the electric field between the tip and the surface. However, little is known regarding the impact of external variables on the mechanism and dynamics of the EF-triggered polymerization/ depolymerization at the solid/liquid interface.

Herein, we explore the impact of solvent. In octanoic acid, the sCOFs are obtained when applying negative sample bias, and the SAMNs are obtained in positive sample bias. Preliminary results show differences when using an aprotic solvent. At the methyl octanoate/highly oriented pyrolytic graphite (HOPG) interface, we haven't obtained the polymerized sCOFs, while depolymerized SAMNs are obtained at both negative and positive sample bias, revealing the role and impact of solvent in the EF-triggered polymerization/depolymerization processes.

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Adsorption and Reactivity of Organic Molecules on the Cu(110)-(2×1)O Striped Phase

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The deposition of molecules onto single-crystal surfaces allows their investigation at the single-molecule level by scanning tunneling microscopy (STM) and gives access to the controllable on-surface synthesis of 2D materials. Here, we have studied dibromo-p-terphenyl molecules on the Cu(110)-(2×1)O striped phase under ultra-high vacuum conditions with low-temperature STM. The Cu(110)-(2×1)O striped phase is of particular interest since it offers alternating stripes of (metallic) copper areas and of oxygen-covered areas where the adsorbed organic molecules are slightly decoupled from the metal substrate and hence have higher mobility.

Previously, the Cu(110)-(2×1)O striped phase was used as a template for the synthesis of organometallic structures having different sizes and shapes depending on the width of copper stripes [1]. The focus of our study is how annealing, which is necessary for covalent polymerization, affects the molecular adsorption on the surface. It turns out that the molecules form organometallic chains on the copper areas, oriented in at least three surface directions. Increasing the sample temperature from 300 K to 450 K induces the reorientation of the organometallic chains into only one surface direction due to embedding in the Cu(110)-(2×1) phase.

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[4+4] Photodimerization of Triptycene Derivatives with Anthracene Blades on Ionic Crystals

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Iptycenes are highly stable compounds with three-dimensional aromatic structures. Derivatives with extended anthracene blades have successfully been self-assembled and subsequently photodimerized both at the air/water interface [1] as well as on various substrates.[2] On metal substrates, it has been shown that reducing the molecule-substrate interaction by iodine-passivation of the Au(111) surface is promoting the formation of large and highly-organized layers with a photopolymerizable arrangement.[3]

In this work, we present the self-assembly of three-fold anthracene-triptycene derivatives without (antrip) and with peripheral fluorine substitution (fantrip) on ionic crystal surfaces. The extended anthracene blades enhance the stability of the supramolecular structures and favor a self-assembly in which all anthracene blades of each monomer are stacked face-to-face. This organization is essential to facilitate the subsequent lateral polymerization by intermolecular [4+4] photocycloadditions. Our results show, that on ionic crystals, both the molecule-substrate and molecule-molecule interaction must be enhanced. This is attained by peripheral fluorine substitution, which increases attractive electrostatic interactions. We discuss, how the deposition and illumination parameters as well as the used ionic substrate can be adapted to optimize the structure quality of the on-surface photo-polymerized 2D polymer.

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Investigation of the wetting layer of $[C_1C_1Im][Tf_2N]$ on Pt(111) by variable temperature scanning tunneling microscopy

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With the introduction of Ionic liquids (IL) novel catalytic concepts like the Solid Catalyst with Ionic Liquid Layer (SCILL) approach have emerged. In a SCILL system, a high surface area solid substrate is covered with a thin IL film, and this film modifies catalytically active surface sites at the support. In order to gain better insights in the underlying effects, it is crucial to obtain a detailed understanding of the IL/solid interface. Due to the low vapor pressure of ILs, these interfaces can be investigated in ultra-high vacuum by surface science methods. Herein, we present our first study on the adsorption behavior of 1,3-dimethylimidazolium bis[(trifluoromethyl)sulfonyl]imide ($[C_1C_1Im][Tf_2N]$) on the reactive Pt(111) surface by variable-temperature scanning tunneling microscopy. We investigated the effect of temperature for coverages up to a closed wetting layer, in particular the formation of 2D islands and their temperature-dependent size. Interestingly, we were even able to detect mobile, single ion pairs on the surface, while for the 2D structures only limited mobility was seen.

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Single-Molecule Mechanics: A nc-AFM and STM Study of Nonahelicene on Ag(110)

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Helicenes are a prominent class of chiral molecules, which have received great attention due to their optical properties [1] and unique surface-aggregation behavior. [2] However, the mechanical properties of these spring-shaped molecules remain unknown, although their macroscopic counterparts are ubiquitous in engineering. To address this issue, scanning tunneling microscopy (STM) and non-contact atomic force microscopy (nc-AFM) measurements were performed with nonahelicene ([9]H) and coronene (Cor) molecules on a Ag(110)-surface. High-resolution imaging with metal and CO-terminated tips revealed then the adsorption structure of isolated and aggregated [9]H molecules on the surface. Interactions of the molecules with a metallic probe tip are quantified by frequency-shift distance measurements under highly controlled conditions (UHV, liq. He). The impact of the helical backbone on the interaction was evaluated subsequently by comparison with flat co-adsorbed coronene. 3D frequency shift maps were then recorded over [9]H-molecules. This molecular deformation mapping (MDM) technique is relevant for the manipulation and chemistry of single molecules and aids here in the resolution of molecular elasticity with submolecular precision.

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Structural Reorientation of Organic Molecules on Surfaces by Alkali Metal Doping

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Organic semiconductors are promising materials for the fabrication of next-generation organic-based electronic devices. In particular, PTCDA molecules are interesting for thin film development due to their rectangular shape and hydrogen bonding. Moreover, the electron properties of the organic thin film can be tuned by alkali metal doping and the consequent charge transfer [1]. Here, we study the influence of Cs doping on the structural and electronic properties of the model system PTCDA/Ag(111). Using a photoemission electron microscope in k-space mode (momentum microscopy mode), we can simultaneously access changes in occupation of the molecular orbitals and determine modifications of the azimuthal orientation of the PTCDA molecules upon Cs doping. We can identify two structural Cs-PTCDA phases depending on the Cs concentration with either one or two Cs atoms per PTCDA. With increasing Cs concentration, we observe a gradual structural reorientation of the molecules that is accompanied by a modification of the population of the molecular states. The intensity maxima in the momentum space at the lowest unoccupied molecular orbit (LUMO) and the highest occupied molecular orbit (HOMO) level indicate that the PTCDA molecules are aligned at 0° and 90° along the [-101] direction of Ag(111) in the case of one Cs per molecule, while they are at 90° in the case of two Cs per molecule. Both cases are different from the pristine case, which has an alignment of 0° and 77° [2]. The structural reorientation of the PTCDA molecules can be attributed to the electrostatic interactions between the partially ionized Cs atoms and the negatively polarized oxygen end groups of PTCDA.

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Non-equilibrium structures of C₆₀ on CaF₂(111)

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Molecular self-assembly on surfaces is widely used as a versatile tool for creating functional structures.¹ These structures are applied in, e.g., catalysis, molecular electronics and sensors.² In classical molecular self-assembly, the preparation is limited to the thermodynamic equilibrium. To enhance the structural variability, morphologies different from the equilibrium structure are desired. We exploit the transition of C₆₀ molecules from the first to the second layer that occurs at a specific temperature to prepare such a non-equilibrium structure.^{3,4}

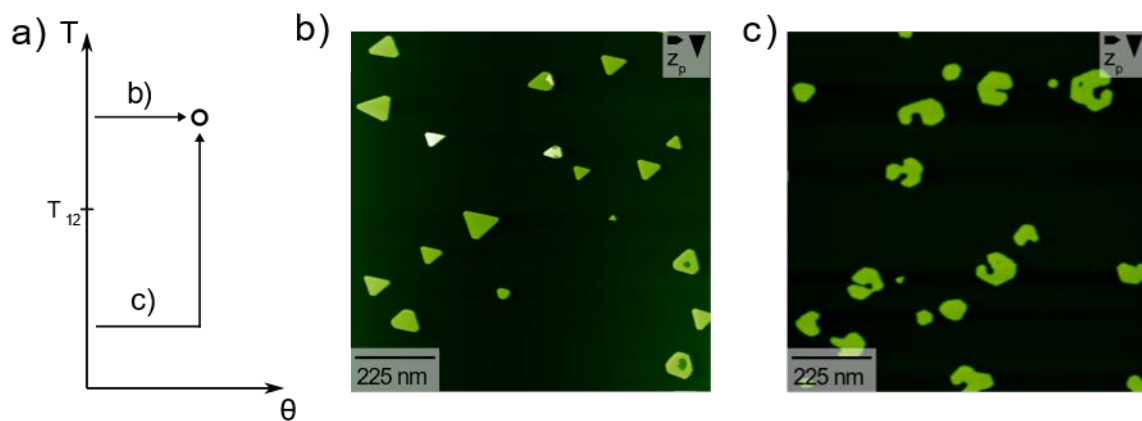


Figure 1: (a) Phase diagram with two different preparation pathways marked in red and blue, respectively. T_{12} denotes the transition temperature. (b) AFM topography images showing the results of these two preparation pathways. The Images are marked with red and blue boxes indicating their corresponding preparation pathway.

Using dynamic atomic force microscopy operated in ultrahigh vacuum, we studied the island morphologies of Buckminster fullerene C₆₀ molecules on the CaF₂(111) surface. We obtained two distinctively different island morphologies by preparing two different pathways (Fig. 1a). Using the first path, islands with a triangular shape are obtained (Fig. 1c). Using the second path islands with a hexagonal shape with characteristic notches are formed (Fig. 1c). In future experiments we will explore this method for creating further morphologies.

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From Aperiodic to Periodic Self-assembly at the Liquid-Solid Interface

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Periodic, long-range ordered two-dimensional (2D) self-assembled molecular networks (SAMNs) have been widely investigated. In this study, the self-assembly behaviour of 4-dodecyl-3,6-di(2-pyridyl)pyridazine (DPP-C12) has been investigated at the heptanoic acid – highly oriented pyrolytic graphite (HOPG) interface using scanning tunnelling microscopy (STM). DPP-C12 forms two types of ordered lamellar structures, however in an aperiodic fashion. (Figure 1) Interestingly, a transformation from aperiodic SAMNs to a periodic one been observed upon the addition of palladium ions (Pd). (Figure 2)

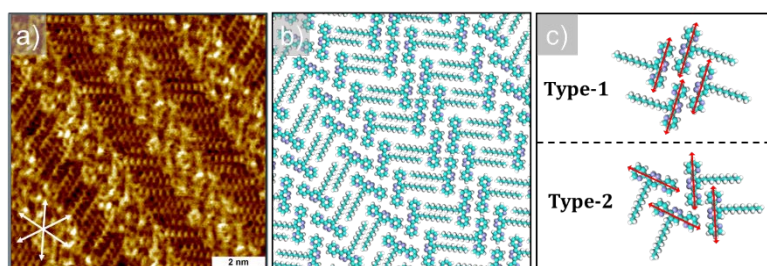


Figure 1. Self-assembly of DPP-C12 at the heptanoic acid (HA) – HOPG interface (a) High-resolution STM images of the adlayer formed by the DPP-C12 at the HA/HOPG interface. (b) Molecular model corresponding to the STM images provided in (a). (c) Two types of packing structures formed by DPP-C12.

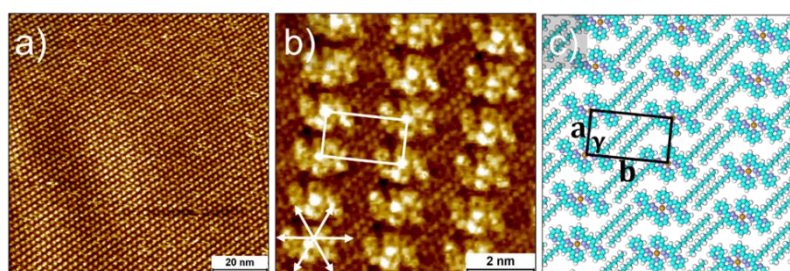


Figure 2. Self-assembly of DPP-C12 at the HA/HOPG interface in the presence of Pd(II) ion. (a) Large-scale STM image of DPP-C12/Pd (b) Small-scale, high-resolution STM images of the adlayer formed by the DPP-C12/Pd molecules at the same interface. (c) Molecular model corresponding to the STM images provided in (b).

Self-assembly and thin film growth dynamics of an ionic liquid on Au(111) investigated in real space

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Ionic liquids (IL) are organic salts with low melting points, often at or even below room temperature. They have shown promise as solvents and electrolytes, but have also become part of novel catalytical concepts involving solid metal catalysts.

In this context, our group studied the self-assembly and growth dynamics of thin films of 1,3-dimethylimidazolium bis[(trifluoromethyl)sulfonyl]imide ([C₁C₁Im][Tf₂N]) on the model surface of Au(111) using scanning probe microscopy[1,2,3]. Our experiments show that the film undergoes distinct phases between the growth of the wetting layer and subsequent multilayers. Further, 2D film growth is shown to be in competition with the growth of a metastable 3D droplet phase, with the dominant growth mode determined by a combination of temperature and nucleus formation.

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Graphene-supported 2D metal organic frameworks with remarkable thermal and chemical stability: Ni-, Fe-, and Mn-TCNQ

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Many potential applications of 2D metal-organic frameworks (MOF) require the systems to be monophase and well-defined at the atomic scale, to be decoupled from the supporting substrate, and to remain stable at the application conditions. Here, we present three systems meeting this elusive set of requirements: M-TCNQ (M = Ni, Fe, Mn) on epitaxial graphene/Ir(111). We study these systems by a combined experimental/computational approach using scanning tunneling microscopy, low energy electron microscopy, x-ray photoelectron spectroscopy and density functional theory computations. When synthesized on graphene, the 2D M-TCNQ MOFs are monophase with $M_1(\text{TCNQ})_1$ stoichiometry; we discuss the structural differences between graphene-supported and metal-supported M-TCNQ systems. We further demonstrate a remarkable chemical and thermal stability of TCNQ-based 2D MOFs: All the studied systems survive exposure to ambient conditions, with Ni-TCNQ doing so without any significant changes to its atomic-scale structure or chemical state. Thermally, the most stable system is Fe-TCNQ which survives flash annealing above 500 °C, while all the tested MOFs survive heating to 250 °C. Overall, the modular M-TCNQ/graphene system combines the atomic-scale definition required for fundamental studies with the robustness and stability needed for applications, thus we consider it an ideal model for research in single atom catalysis, spintronics or high-density storage media.

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Spin Switching in Self-Assembled Tetramers on Ag(111)

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Spin-crossover (SCO) molecules can be switched between a low spin (LS) state and a high spin (HS) state. Adsorption to a surface can lead to a drastic change of the SCO behaviour. While selective, electron-induced switching of single SCO molecules has already been reported little is known about molecules that interact in twodimensional arrays. We present a low-temperature scanning-tunneling-microscope investigation of the switching characteristics of metal-based SCO molecules organized in tetramers on a Ag(111) surface^{1,2,3}. Via the injection of current pulses two molecules per tetramer can be reversibly switched¹. In addition, these molecules may be switched remotely by applying the excitation to one of the other two molecules of the tetramers. The latter molecules themselves are immutable. We induced tens of thousands of switching events using different currents and voltages and observed that the switching yields that are 2 to 3 orders of magnitude larger compared to previous results. We show that the switching is likely linked to a spin transition and also report three-state switching that involves charging of a molecule². A preliminary model of the electronic transitions³ involved in electron-induced switching is presented.

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Charge-state lifetimes of single molecules on ultrathin insulating films

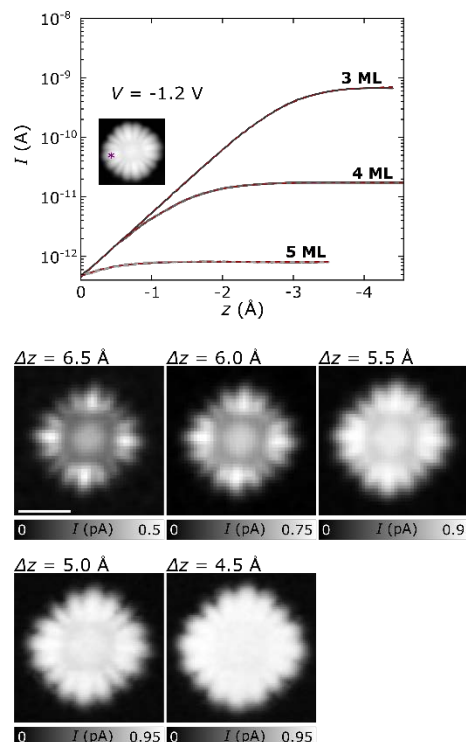
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In scanning tunneling microscopy (STM) experiments of molecules on insulating films, tunneling through molecular resonances goes along with transiently charging the molecule. The transition back to its charge ground state by tunneling through the insulating film crucially determines the charging dynamics of the system and with this is essential for understanding, for example, excited state formation and luminescence quenching in electroluminescence experiments. The two quantities describing these processes are the average charging and discharging time, the latter being the lifetime of the charged state, and they are accessible in STM experiments: By approaching the tip to the molecule at resonant tunnel conditions up to a regime where charge transport is limited by tunneling through the NaCl film the saturation of the tunnel current (see Figure), which is a direct measure of the molecule's charge-state lifetime and thus provides a means to study charge and exciton dynamics, can be measured. We report on the charge-state lifetimes of individual molecules adsorbed on NaCl films of different thicknesses on Cu(111) and Au(111), and provide insights into the role of the substrate and the spacer layer.



Top: Current as a function of tip-height for ZnPc adsorbed on NaCl films of different thicknesses on Au(111).

Bottom: Constant-height STM images at different tip-height offsets (Δz) on ZnPc adsorbed on 5ML NaCl on Au(111).

Both is recorded at -1.2 V.

Distance dependence of *s*- and *p*-wave contributions in CO-tip STM

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Functionalized tips are frequently used in high-resolution AFM, particularly CO terminated tips, to facilitate atomic resolution [1]. CO functionalized tips can also enhance contrast in STM measurements of ionic resonances, mapping orbital densities [2,3]. For CO tips both *s*- and *p*-wave character of the tip contribute to the contrast [3,4,5]. Here we study the contributions of *s*- and *p*-wave character of CO tips as a function of tip height, bias voltage and tunneling current.

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Polymerization of silanes via dehydrogenative Si–Si bond formation on metal surfaces

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In on-surface synthesis, reactions between organic molecules via C-C bond formation has become one of the most popular approaches for the preparation of one-dimensional polymers, graphene nanoribbons, and two-dimensional nanomaterials ^[1]. As a higher homolog element of carbon in group 14, silicon also is highly valuable in organic chemistry and nanomaterials, but the diversity of its functional groups is still limited compared to carbon. Here, we demonstrated Si–Si bond formation in on-surface chemistry. Polymerization upon multiple Si–H bond dissociation and subsequent Si–Si bond formation was achieved on the Au(111) and Cu(111) surfaces by using two different monomers, each containing two silicon functional groups (CH₃SiH₂ or SiH₃) attached to an aromatic backbone, leading to polymeric disilenes that interact with the surface ^[2]. Non-contact atomic force microscopy (nc-AFM) with qPlus sensor ^[3] and a functionalized Oxygen-terminated Cu-tip ^[4], and X-ray photoelectron spectroscopy (XPS) measurements combined with density-functional theory (DFT) calculations were performed to corroborate the formation of covalent Si–Si bonds. The reactive Si–Si double bonds formally generated via double dehydrogenative coupling are stabilized by the metal surfaces. It opens a new avenue to preparing one- or two-dimensional silicon-organic materials on surfaces that have potential applications in nano-electronic devices due to their optoelectrical property and the new type of molecule-surface junction.

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On-Surface Strain-Driven Synthesis of Nonalternant Non-Benzenoid

Aromatic Compounds Containing Four- to Eight-Membered Rings

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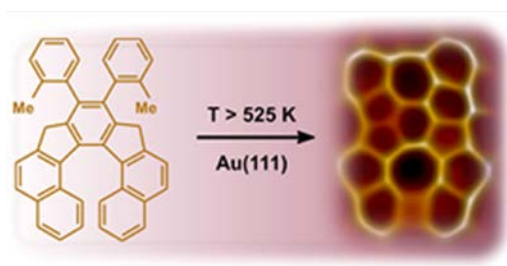
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Synthesis of polycyclic aromatic hydrocarbons containing various non-benzenoid rings remains a big challenge facing contemporary organic chemistry despite a considerable effort made over the last decades [1]. Herein, we present a novel route [2], employing on-surface mechanochemistry, to synthesize non-alternant polycyclic aromatic hydrocarbon containing up to four distinct kinds of non-benzenoid rings. We show that the surface-induced mechanical constraints imposed on strained helical reactants play a decisive role leading to the formation of products, energetically unfavorable in solution, with a peculiar ring current stabilizing the aromatic character of the π -conjugated system. Determination of the chemical and electronic structures of the most frequent product reveals its closed-shell character and low band gap. The present study renders a new route for the synthesis of novel non-alternant polycyclic aromatic hydrocarbons or other hydrocarbons not available by traditional approaches of organic chemistry in solution.



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Tailoring electronic and magnetic properties of metal-organic coordination networks by lanthanide exchange

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Lanthanides are appealing for the design of on-surface metal-organic networks. The inner nature of their valence electrons, together with their high spin-orbit coupling, leads to high magnetic anisotropy barriers [1]. Combined with the versatility to form coordination structures, the employment of lanthanides allows metal-organic architectures with a huge variety of structures and physical properties [2].

In this work [3], we present a study of the synthesis, electronic and magnetic properties of Dy- and Er-based coordination networks featuring binuclear nodes, by coordinating ditopic linear ligands equipped with pyridyl groups (DPBP) with Dy/Er atoms on a Au(111) substrate. To this aim we have taken advantage of STM, XAS, XMCD and XLD, complemented with DFT and multiplet calculations.

Our results show that Er- and Dy-directed assemblies feature identical structural architectures. Notably, despite exhibiting the same +3 oxidation state, there is a shift of the energy level alignment of the unoccupied molecular orbitals between Er- and Dy-directed networks. In addition, there is a reorientation of the easy axis of magnetization and an increment of the magnetic anisotropy when the metallic center is changed from Er to Dy. These findings pave the way to the design of lanthanide-based metal-organic networks with tunable properties through lanthanide exchange.

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Interaction of a novel strong organic electron acceptor with Au(111): can SPM and DFT be enough to investigate the presence of adatoms in metalorganic frameworks?

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Molecular doping is a well-established procedure to develop tailored and highly-efficient active materials in organic electronics and photovoltaics. Organic systems with increasingly stronger acceptor behaviour have been developed in recent years and their characterisation by fundamental analytical approaches is key to understand their behaviour in future applications. Herein we present the results of a combined scanning tunnelling microscopy (STM), spectroscopy (STS) and density functional theory (DFT) study on hexacyano-trimethylene-cyclopropane (CN6-CP), a new electron acceptor molecule with an unprecedented high electron affinity, displaying the deepest LUMO reported so far for an organic molecule.

Due to its extremely low-lying LUMO, CN6-CP is a highly unstable species, prone to rapid reduction in both ambient and solution conditions. A protocol was found to successfully evaporate it in ultra-high vacuum on a Au(111) substrate and image it at 77K. STM results show that CN6-CP self-assembles in a commensurate hexagonal ordered structure. The inclusion of gold adatoms is strongly suggested by the STM images. DFT simulations have been performed to verify the validity of the adatom hypothesis and to investigate the density of adatoms per unit cell, while Tersoff-Hamann simulations have provided a reference for the experimental results. Bias dependent STM imaging, local STS, and dI/dV imaging indicated the filling upon adsorption of the gas-phase LUMO. A high inhomogeneity of the electronic characteristics of CN6-CP within the self-assembled islands was also observed. In particular, we recorded significant variations in the HOMO-LUMO gaps in neighbouring molecules, suggesting a highly complex energy level alignment at the metal-organic interface. DFT calculations to further investigate the structural and electronic characteristics of the system have been carried out to understand this behaviour.

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I have been hoping to take part to this meeting since early 2021, when I was still just a PhD student, as I feel that this seminar is the perfect opportunity to deepen my knowledge on the current cutting-edge research in the field and broaden my general understanding of molecule-functionalised systems, as a young researcher focusing on the characterisation at surfaces of polymeric systems and their molecular dopants. I

hope I will actively be able to contribute to the meeting by presenting my results, and to provide exciting insight on a system that is still poorly understood, but relevant to direct applications in organic electronics. I also hope to be able to interact with students, fellow young researchers, and more experienced scientists.

Phenyl- trioxatriangulenium on Au (111) studied with low-temperature scanning tunneling microscopy

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The functionalization of surfaces is a first step to realizing sophisticated applications such as chemical sensors, molecular machines and catalysts. We use the molecular platform trioxatriangulenium (TOTA) that features a central carbon atom to which functional groups can be vertically attached. Here we investigate phenyl-TOTA with low-temperature scanning tunneling microscopy. The molecules are sublimated onto Au (111) at ambient temperature. We find that 99 % of the molecules remain intact after sublimation. The platforms arrange into hexagonal and honeycomb arrays, preferentially in fcc areas of the reconstructed Au substrate. They may also conveniently be moved with the STM tip. We show first spectroscopic results and also present current-distance measurements that cover the transition from tunneling to a single molecule contact.

Unveiling the Formation Mechanism of the Biphenylene Network

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The rational synthesis of carbon allotropes has been achieved by designing appropriate molecular building blocks to undergo surface-assisted C-C coupling under ultrahigh vacuum conditions after deposition on a crystalline substrate. Extensive efforts have been devoted into constructing C-C bonds via different on-surface reactions. Nevertheless, only graphene has been realized as a purely hexagonal net, while the synthesis of other planar carbon allotropes consisting of non-hexagonal geometry is very limited. Very recently, a reliable protocol for synthesizing non-hexagonal planar carbon allotropes has been developed, in which the C-C coupling via the intermolecular HF zipping reaction has been realized experimentally.[1] The generated biphenylene networks (BPN) consist of periodically arranged four-, six-, and eight-membered rings, and exhibit an uncommon metallic conductivity. Despite the success in experiment, the underlying mechanism for the formation of BPN still remains unclear. Therefore, it is crucial to provide a comprehensive theoretical understanding of the intermolecular HF zipping for the further development of such on-surface synthesis protocol.

In this work, we have theoretically investigated thermodynamic properties and reaction kinetics of intermolecular HF zipping on the Au(111) surface. Despite the HF zipping is highly endothermic, the entropy contribution of dissociated HF molecules makes the reaction thermodynamically favored. The most favored reaction pathway has been identified, consisting of three main stages: defluorination, dehydrogenation, and the C-C coupling. The defluorination and dehydrogenation are found to proceed consecutively, while the C-C coupling is identified as the rate-limiting step. As a result, an intermediate state comprises of C-Au bonds, resulting in “standing” benzyne groups on the surface, has been identified from both theoretical calculations and experimental observations. Furthermore, such standing benzyne groups can effectively reduce the energy barrier of subsequent C-C couplings, making the formation of large-scale networks possible.

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Plasmon-Induced Molecular Manipulation of PTCDA on Si(111): An STM-TERS Study

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We studied a unique plasmon-induced molecular motion of perylenetetracarboxylic dianhydride (PTCDA) single molecules on the Si(111)-7x7 surface by means of the atomic point contact (APC) tip-enhanced Raman spectroscopic (TERS) measurements with a low temperature scanning tunneling microscope (STM) under an ultrahigh vacuum condition. In our APC-TERS scheme, a silver tip approaches close to the molecule or the surface until the tip makes an atomic point contact with its counterpart. It was reported by our previous study that at the point contact with Si(111) surface the TERS signal was significantly enhanced.^[1] The PTCDA single molecules on the Si(111), which are fixed on the surface by four oxygen-silicon bonds, showed a distinctive APC-TERS pattern where the Raman intensity was dramatically enhanced at a certain gap distance range during the tip approach, and then was attenuated back at shorter tip-molecule distances. This “sweet spot” pattern was reversibly observed during the tip retraction. The “sweet spot” had a different spectral pattern from that of bulk PTCDA molecular films or that of flat-lying molecules on Si(111). At the “sweet spot”, the STM current rapidly switched (<20 ms period) with large amplitudes, which implies a fluctuative motion of PTCDA molecule at the junction. The fluctuation is derived by interaction of the molecule with a tip plasmon, not solely by the laser irradiation, as the laser irradiation did not result in such current switching and “sweet spot” with the tips that had no plasmonic response. Besides, the Raman intensities were proportional to the current switching amplitude. We were able to perform a tapping-mode-like line-profiling utilizing the TERS “sweet spot”, which showed >3 Å lateral spatial resolution. We believe this unique system could provide a better understanding on the plasmon-molecule interaction and the plasmon-induced molecular manipulation, as well as their implication on the enhancement mechanism in TERS.

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Pathway to Achieve Tunable Single Molecule Light Emitting Sources

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Scanning tunneling microscopy (STM) proved to be a unique bottom-up technique in order to control and understand light emitting processes from a single molecule. In this work, based on two examples, we show how STM can be used to improve molecular designs to achieve single self-decoupled molecules capable of emitting light into the far field. In the first example, we show that fully fluorescence quenched 2,6-core-substituted naphthalene diimide derivatives in a self-assembled monolayer directly deposited on an Au(111) surface can be activated with the tip of a scanning tunnelling microscope to emit light. The observed light emission efficiency compares to the previously observed only by use of decoupling layers such as NaCl. In the second example, we show that the same chromophores mounted on newly designed tripodal molecular platforms adsorbed on a gold surface present well-defined and efficient electroluminescence down to the single-molecule level without the need of any manipulation from the STM tip. Light emission from such single self-decoupled molecules directly adsorbed on a metal substrate opens up a pathway to study a wide range of functional molecules for the further development of highly efficient and tunable photon emitters.

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Autonomous single-molecule manipulation based on reinforcement learning

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The physics that govern manipulating molecules on a surface via STM tip induced electric fields is complex and involves the interaction between the tip and the molecule as well as the molecule and the substrate.¹ Attempting to precisely control molecules, such that they form defined nanostructures, is therefore a complex, repetitive, and time-consuming task.

Here, we show a reinforcement learning algorithm that learns how to control a single dipolar molecule in the presence of an electric field. Within about 2250 training iterations, the algorithm learns to manipulate the molecule towards arbitrary positions on the surface.

In parallel, the algorithm allows to visualize the underlying model and generates important insights into the movement of the molecule and why specific manipulations re-orient and translate the molecule. This reveals that molecular movement is strongly inhibited in some directions and the torque on the dipole due to the electric field is not symmetric around the dipole moment. These findings can be analyzed post-hoc and reveal how electric fields dynamically affect molecules adsorbed on metal surfaces.

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Surface-Assisted and Solvent Dependent Elimination of Redox-Active Axial Ligand from Metal Porphyrin

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The surface-assisted axial deligation of a porphyrin molecule adsorbed on graphite surface is studied by scanning tunneling microscopy. Present study involves supramolecular self-assembly of 2,3,7,8,12,13,17,18-octaethylporphyrin iron(III) chloride [FeOEP(Cl)] on graphite surface. It is demonstrated that when FeOEP(Cl) solution in heptanoic acid was drop-casted onto a graphite surface, two different kind of species are observed in STM images. The central part of the few molecule appears as bright whereas in some molecules a depression in STM images. Bright molecules is identified as a FeOEP-Cl molecule with the chlorine atom oriented away from the surface, whereas dim molecules are assigned as the dechlorinated FeOEP. Overall, on graphite surface, partial dechlorination was observed and, therefore, a change in the oxidation state of iron. The effect of nature of solvent, various tunneling parameters (set point & bias voltage), and voltage pulse on number of chlorinated/dechlorinated molecules as well as on self-assembly was also investigated.

Synthesis and Chiral Resolution of [2.2]Paracyclophane derivatives on HOPG surface: Self-assembled monolayer of 3D nanostructure

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Since the discovery of chirality, interest in this subject has grown exponentially. While the study of 3D chirality has been studied for a long time, the interest in surface chirality has developed only in the last few decades. The driving force for this new type of chirality is the need to develop a new functionalized chiral surface for enantiospecific application¹. In this work, we focused on [2.2]Paracyclophane (PCP) a fascinating molecule that offers great potential in a wide range of applications². The PCP-based building blocks are easy to functionalize and have a defined 3D nanostructure. The presence of the two-benzene ring in a sandwich-like disposition allows the exact positioning of vertical structural elements^{3,4}. Using the well-known chemistry of PCP we functionalize this molecule. Herein, scanning tunneling microscopy (STM) was employed to investigate the surface chirality of racemic and enantiopure PCP derivatives in self-assembled domains at the solution/solid interface. Current analysis has shown different domains that can be related to the homochiral aggregation of the racemic adsorbate.

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Synthesis and Characterization of Magnetic Aza-Triangulene Nanostructures

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The emergence of spin states in triangular-shaped graphene fragments with zig-zag edges (triangulenes) is a conceptually attractive theoretical proposal from a decade ago. Thanks to the recent development of on-surface synthesis strategies, triangulene nanostructures can now be fabricated on metal substrates with atomic precision. Their potential application in graphene-based spintronics and molecular devices is a milestone toward next-generation technology.

On-site Coulomb repulsion induces a net spin-polarization, breaking the degeneracy of zero-energy eigenstates of the tight-binding framework. This form of degeneracy lifting is favored by π -electron hybridization in the bipartite sublattice. Thus, unpaired electrons in these flakes show parallel magnetic ordering. The precise spin state of these open-shell molecules can be tailored by their size or via heteroatom doping.

In this work, we present the synthesis and characterization of [5]-Aza-triangulene (A5T) and Tri-anthracene-[3]-aza-triangulene (TATAT) on Au(111) surface. Theoretical models predict such structures to have more than two unpaired electrons, which could result in larger spin states. Combined scanning tunnelling microscopy (STM), and atomic force microscopy (AFM) measurements using CO-functionalized tips confirm the precise structure of the triangular flakes. Scanning tunnelling spectroscopy (STS) was used to directly prove the magnetic ordering by measurements of the Kondo effect or spin excitations. Experimental findings are further corroborated by the predictions of theoretical models such as density functional theory (DFT), mean-field Hubbard model (MFH), and Heisenberg model. The N heteroatom substitution not only modifies the spin state of the pristine molecule but also affects the interaction with the underlying gold surface. Phenomena such as charge transfer to the metallic surface and Jahn-Teller distortion take on even greater importance with respect to non-doped nanographene structures.

Funneling energy at the molecular scale

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Resonant energy transfer (RET) plays a critical role in natural and artificial light-harvesting complexes (LHC) as a mechanism enabling optimized and directed funneling of energy from the collection to the reaction centers. The overall efficiency of this process depends on each individual RET step, which is controlled by the chemical nature of the participating chromophores, their relative distances and environment with their relative roles still being intensively debated. Because these parameters inherently depend on the atomic-scale properties of matter, probing and controlling them at the level of an individual system remains a challenge.

We address this issue by profiting from the atomic-scale precision of scanning tunneling microscopy (STM) [1]. First, STM allows us to build “by-hand” artificial dimers and trimers consisting of phthalocyanine chromophores. Second, thanks to STM-induced luminescence we are able to probe electroluminescence of the chromophores with sub-molecular precision and observe RET at its natural spatial scales. On an individual dimer level, this approach enables us to probe RET efficiency as a function of the chromophore separation, relative dipolar orientation, including selective dipole excitation, and chemical nature of the molecule. Using trimers, where chromophores are arranged in different ways with respect to their optical band gap, we control the energy funneling by playing with the role of the intermediate molecule that can act as an ancillary, passive and trap molecule, all of which act as non-covalent RET bridges enabling long-range RET. Relying on organic chromophores as elementary components, our approach constitutes a powerful model to address fundamental physical processes at play in natural LHC.

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Atomic forces and relaxations in single-molecule reactions

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We combine atomic force microscopy (AFM) experiments on single phthalocyanine (Pc) molecules adsorbed on Ag(111) with density functional theory (DFT) simulations to probe structural relaxations upon the atom-by-atom abstraction of pyrrolic H, to gain insight into the subsequent on-surface metalation with a single Ag atom and the bonding behavior of the resulting two conformational Ag-Pc isomers with a CO-terminated AFM tip.

The atomwise abstraction of pyrrolic H leaves its footprints in spatially resolved force spectra with a CO-terminated tip. The magnitude of the point of maximum attraction unveils the macrocycle center as the most attractive region of the molecule; its vertical shift towards the substrate surface upon moving from the molecular periphery to the center matches well DFT predictions of the relaxed adsorption geometry.

On-surface metalation of a single free-base Pc is achieved by adding a single Ag atom from the AFM tip to the macrocycle center. Lower bounds of the force and energy for the metalation process can be inferred from probing the force variation at the verge of the chemical reaction. The spontaneous atom transfer is in agreement with the DFT energy profile determined in a nudged-elastic-band approach.

The metalation leads to two conformational isomers with clearly distinct bonding behavior to an approached CO molecule. The isomer with the central Ag atom pointing to CO (Ag-Pc \uparrow) exhibits a complex evolution of the distance-dependent interaction, while the conformer with Ag bonded to the metal surface (Ag-Pc \downarrow) gives rise to a Lennard-Jones behavior. Simulations within DFT comprising the entire junction highlight the role of structural relaxations, physisorption and chemisorption for Ag-Pc \uparrow , while Ag-Pc \downarrow exhibits chemical inertness to the bonding with CO.

Local Work Function of Graphene Nanoribbons

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Graphene nanoribbons (GNRs) exhibit remarkable electronic properties due to local confinement [1]. Differences in structural and electronic properties can occur caused by the underlying substrate. We have investigated the variation of the local contact potential difference (LCPD) of the GNRs on the Au(111) surface using frequency modulation scanning force microscopy (FM-SFM) in ultra-high vacuum. The LCPD images were acquired by parallel recording of topography and frequency modulation Kelvin Probe Force Microscopy (FM-KPFM). The LCPD images reveal a charge transfer between the GNRs and the underlying substrate and confirm the p-type doping of the GNRs on Au(111) [2]. We have prepared the GNRs via on-surface synthesis on a Au(111) substrate [3]. The precursor molecule 10,10'-dibromo-9,9'-bianthracene (DBBA) was vapour-deposited onto the Au(111) at 470 K and then held at 470 K for 10 min for dehalogenation. The dehydrogenation takes place during a second annealing step at 670 K. Density functional theory (DFT) calculation supports the experimental findings.

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Photoactivity of anhydrides on a semiconductor surface

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During the last decade the on-surface synthesis field has emerged, overcoming some intrinsic limitations of conventional solution synthesis, giving rise to the formation of unprecedented carbon-based nanomaterials on noble metal surfaces. Recently, on-surface synthesis has been expanded to the study of chemical reactions on inert surfaces in view of the requirements needed for technological applications, where the absence of a metal surface that catalyzes the chemical reaction makes it challenging. The adsorption energy on inert surfaces is lower than on metal surfaces, which limits the viability of thermally activated reactions. Typically, molecular desorption upon thermal activation on inert surfaces takes place before carbon-carbon coupling occurs, thus, another alternative as photochemistry has to be considered^[1]. Here, we present the selective photoactivation of tetraphenyl phthalic anhydride (TPPA) on an inert SnSe surface grown on Au(111). Upon irradiation of the TPPA on SnSe with UV-light at room temperature we observe the photo-induced decarboxylation and decarbonylation of the molecules^[2,3]. The structural and electronic characterization of the tetraphenyl ortho-benzyne was performed by scanning tunneling microscopy (STM) together with density functional theory (DFT) calculations.

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LT-STM induced reversible switching of thiophene based molecule on Au(111)

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In the ongoing quest for miniaturization of machines, single molecule machinery holds a plethora of possibilities. Advancements in nanoscale imaging techniques, such as Scanning Tunneling Microscopy and Spectroscopy (STM, STS), allows not only the addressing of single molecules individually but through tunneling electrons/electric field stimulation with an STM tip, one can experimentally study fundamental properties of molecules such as pi-conjugation and charge transfer to a surface, and the effect it has on the switching behavior. We present the design and synthesis of a nanoswitch which exhibits a reversible switching from achiral to chiral mode on Au(111). The electronic states of both conformations have been measured with a high degree of spatial resolution, thereby showing the pathways of the electron-induced isomerization. Furthermore, we demonstrate this effect being suppressed on Ag(111).

Molecular-substrate systems studied by scanning tunnelling microscopy: Spatial, energetic, and temporal resolution

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The self-assembly and on-surface reactivity of molecular species is central to the concept of devices which incorporate the functionality of molecular components. Materials with specific catalytic, electronic, optical, and/or magnetic properties can, in principle, be realised by appropriate choice of molecular-substrate systems. However, preparation of such materials requires an understanding of the processes which give rise to ordered molecular arrays and, in the case of covalently organic frameworks (COFs), the mechanics underlying the observed on-surface chemistry.[1] Ultra-high vacuum (UHV) scanning probe microscopy (SPM) approaches allow on-surface processes to be studied on the single-molecule and single atom level, [2] and in combination with photoemission spectroscopies can provide detailed structural and chemical characterisation.[3]

Here we present details of our recent scanning tunnelling microscopy (STM) work characterising the energetic, and spatial, distribution of the electronic states within cyclic porphyrin polymers is possible.[4] The high lateral resolution of STM, combined with the electronic characterisation offered by differential conduction maps, provides unique information on these materials. A similar approach allows identification of chemical groups within single molecules and extended molecular structures for Br functionalised porphyrins. Additionally, our temperature-dependant SPM measurements provide information on the dynamics and energetics of on-surface diffusion and reactivity of porphyrins; with synchrotron-based photoelectron spectroscopies (e.g. XPS and NEXAFS) quantifying chemical changes within on-surface reaction processes.[5]

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Unusual Diffusion and Island Evolution in Pb/Si(111)-(7x7)

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Pb islands on silicon show a wide range of interesting properties. Previous work has already been able to explain some features, such as the unusual height distribution of the islands[1,2]. The growth of the islands should be described by random walk diffusion. Indeed the Pb-islands growth in a “explosive” way, which is too fast to be explainable by this type of diffusion [3,4]. The development of the Pb islands by diffusion was investigated. We also try to understand in wetting layer, when we observe growth and decay of the islands. For the investigation, we have used scanning force microscopy in the non-contact frequency modulation mode and Kelvin probe force microscopy measurements in ultrahigh vacuum between 120K and room temperature. The Si has been cleaned by direct current heating. Subsequently, Pb has been vapor deposited on Si at various temperature. During the measurement, the cooling was subsequently stopped. AFM and KPFM measurements were performed simultaneously over several hours.

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Atomic-scale and electrochemical characterization of catalytically active triazine-based copper nitrides

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Due to their reduced coordination, singly dispersed metal atoms can exhibit beneficial catalytic properties for an increased chemical reactivity and reaction selectivity. In turn, to gain sufficient stability against agglomeration and for the formation of single atom catalysts (SACs) supramolecular structures can be used. [1] In our approach [2], we use single copper atoms embedded in a supramolecular network based on reacted layers of melamine and melem. The metal-organic layers are prepared on Cu(111) by on-surface synthesis. Via heat-induced dehydrogenation of the precursor molecules the metal-coordinated bonds are formed. These layers are characterized by non-contact atomic force microscopy (nc-AFM), X-ray photoelectron spectroscopy and ab-initio DFT simulations. Our investigations reveal an extremely strong molecule-substrate interaction after complete dehydrogenation. This leads to a highly unusual adsorption configuration with significantly reduced adsorption heights as compared to physisorbed molecules.

The terminating oxygen atom of the used functionalized nc-AFM tip [3,4] shows strong interactions on the intermolecular N-Cu-N sites. Corresponding DFT simulations confirm extremely lifted copper atoms and pronounced interactions with oxygen species. This indicates a catalytical activity of the on-surface synthesized supramolecular copper nitride layers. Their actual catalytic performance is investigated by a custom-made setup for cyclic voltammetry experiments on the single crystal where we found a robust irreversible reduction of oxygen.

This approach correlates the atomic-scale characterization by AFM with a direct electrochemical proof of performance in the technologically highly relevant oxygen reduction reaction. Therefore, it constitutes an important progress in the fundamental understanding of active sites in electrocatalytic processes.

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Visualization of *D*- and *L*-glycan assemblies and their interactions by high-resolution scanning tunneling microscopy

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The main molecular building blocks of life appear predominantly in one handedness. Among these, glycans are the most abundant biomolecules and play important roles in areas ranging from sustainable and environmentally friendly materials to cellular processes and cell recognition. However, characterization of glycans and their interactions at the nanometer scale remains elusive. Only recently, mass-selective, soft-landing electrospray ionization deposition of glycan molecules and their subsequent characterization by scanning tunneling microscopy (STM) under ultra-high vacuum conditions at low temperatures has emerged as characterization tool for glycan molecules with real-space information down to the single glycan unit level, but no intramolecular details of the single glycan units could be resolved so far.

Here, we use high-resolution STM imaging to visualize intramolecular details of *D*- and *L*-cellohexaose as well as interactions between the molecules. By modifying the STM tip with a CO molecule and using constant-height scanning, the improved resolution reveals additional intra- and intermolecular details. That is, a correlation between high-resolution STM contrast and the expected position of intramolecular hydrogen bonds is observed. Two types of glycosidic bonds are resolved, which differ in the orientation of the oxygen in the bond. In extended assemblies, dimer formation is observed with a sharp feature in the STM contrast at the position of hydrogen bonds between the molecules in the dimers.

Further, the observed contrast shows chiral features and thus allows the differentiation between *D*- and *L*-cellohexaose on the single glycan unit level. The deposition of enantiopure *D*- or *L*-cellohexaose reveals their assembly in mirror-symmetric chiral patterns and the deposition of a racemic mixture revealed conglomerate formation, which is, to the best of our knowledge, the first example of a crystallization-based separation of racemic glycans.

On-surface synthesis of nonplanar polymer chains containing oxygen functionalized pores

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Porous graphene-based nanostructures have recently attracted much attention due to various potential applications, including water desalination, gas separation, ion transport, and sensing. Here, we explore a synthetic strategy for the preparation of nonplanar porous polymer chains bearing oxygen functionalized pores from predesigned 4,5,9,10-tetrabromo-2,7-dioxa-1,3,6,8(1,4)-tetrabenzacyclodecaphane monomers on Ag(111) and Au(111) using low-temperature scanning tunneling microscopy and X-ray photoelectron spectroscopy(XPS). First, we will discuss the self-assemblies of the precursors upon adsorption on the metal substrate. Second, we show that the terminal H and Br functional groups provide for different reaction pathways and reaction products on coinage metals. On Au(111), covalent chains are formed upon annealing, while on Ag(111), metal-organic chains are observed as intermediates before the covalent-linking of the precursors. The different reaction pathways lead to different bonding motifs between the molecules on Au and Ag and, thus, to different chain structures on both surfaces.

Emergence of a singly-occupied state of *p*-terphenyl-based thiols bound to sulphur defects on MoS₂/Au(111)

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The combination of transition-metal dichalcogenides (TMDCs) and organic molecules into hybrid inorganic-organic systems is a field gathering much interest in recent years. The use of submonolayers of the TMDC MoS₂ as a decoupling layer in an STM junction is already well established and allows highly resolved dI/dV spectra. But 2D materials also have drawbacks: Their properties are highly dependent on their local structure, because defects influence their properties severely.

Here we utilise these defects by anchoring the thiol-based molecule CF₃-3P-SH (trifluoromethyl-*p*-terphenyl-thiol) into purposely created top-layer sulphur point defects in MoS₂ on Au(111). One end-group of the anchored molecule is bound to the defect, allowing it to rotate around the anchoring point. On such molecules we observe a Kondo resonance. *Ab initio* molecular dynamics simulations show the emergence of a singly-occupied molecular state near E_F depending on the configuration of the molecule with respect to the surface, which in turn gives rise to the observed Kondo resonance.

Aza-Triangulene and its fused dimers on surfaces

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Nitrogen heteroatom doping into a triangulene molecule allows tuning its magnetic state. However, the synthesis of the nitrogen-doped triangulene (aza-triangulene) has been challenging. Herein, we report the successful synthesis of aza-triangulene and its fused dimers on the Au(111) and Ag(111) surfaces, along with their characterizations by scanning tunneling microscopy and spectroscopy in combination with density functional theory (DFT) calculations [1]. Aza-triangulenes were obtained by reducing ketone-substituted precursors. Exposure to atomic hydrogen followed by thermal annealing and, when necessary, manipulations with the scanning probe afforded the target product. We demonstrate that on Au(111), aza-triangulene donates an electron to the substrate and exhibits an open-shell triplet ground state. This is derived from the different Kondo resonances of the final aza-triangulene product and a series of intermediates on Au(111). Experimentally mapped molecular orbitals match with DFT-calculated counterparts for a positively charged aza-triangulene. In contrast, aza-triangulene on Ag(111) receives an extra electron from the substrate and displays a closed-shell character. In addition, the electronic and magnetic properties of various fused aza-triangulene dimers obtained by further annealing on Au(111) have been also investigated. The charge transfer trend keeps the same as monomers and these aza-triangulene dimers are supposed to hold only one unpaired π electron. Interestingly, the magnetic properties of aza-triangulene dimers on Au(111) show strong dependence on the molecular symmetry. In contrast to the sharp Kondo resonance exhibited in asymmetric dimers, larger spin delocalization in the symmetric dimer gives rise to a smaller Coulomb gap and thus partial occupation of HOMO instead of exhibiting SOMO-SUMO splitting and associated Kondo resonance.

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Self-Assembly and Single-Molecule Manipulation of Borazine on Ag(111)

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Borazine ($B_3N_3H_6$), a cyclic molecule isostructural with benzene, is a prominent precursor for the growth of hexagonal boron nitride (hBN) on metal supports[1]. With monolayer hBN playing an important role in the thriving field of two-dimensional materials, borazine adsorption, assembly and decomposition on surfaces is a topic of interest. For example, earlier space-averaging experimental studies combined with theoretical modeling revealed flat adsorption geometries on rather inert substrates whereas tilted adsorption configurations occur upon dehydrogenation on substrates with higher catalytic activity [2,3].

Here, we provide for the first time real-space insight into adsorbed borazine molecules and their on-surface chemistry. Specifically, we report on the self-assembly of borazine on Ag(111) which was investigated by LT-STM. A highly regular, porous hexagonal assembly and a denser-packed structure are observed for low- and high-exposure experiments, respectively. Both phases feature chiral domains, where borazine adsorbs with the ring parallel to the surface. Furthermore, dehydrogenation reactions of single borazine molecules can be induced by the tip of the STM. This manipulation protocol yields products with distinct appearance in the STM data, attributed to tilted adsorption geometries. Complementary DFT calculations were performed to rationalize the experimental data and to comprehensively characterize potential adsorption configurations.

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Fabrication and Characterization of 2D Metal-Organic Frameworks on Weakly Interacting 2D Materials

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The fabrication of atomically precise structures with designer electronic properties is currently being vigorously pursued within condensed-matter physics and materials chemistry research communities [1]. Over the past two decades, low-dimensional metal-organic frameworks (MOFs) with various atomically precise lattice structures have been fabricated on coinage metal surfaces [2]. Recently, our group has synthesized and characterized several two-dimensional (2D) MOFs on the weakly interacting substrates under ultra-high vacuum (UHV) conditions using low-temperature scanning tunneling microscopy (STM) and spectroscopy (STS) [3-5]. We demonstrate a successful synthesis of a large-scale monolayer Cu-dicyanoanthracene (DCA) network that can grow across the terrace of an epitaxial graphene surface [4]. The ordered DCA₃Cu₂ network shows a structure combining a honeycomb lattice of Cu atoms with a kagome lattice of DCA molecules. Combining the STM/STS data with density-functional theory (DFT) results, we confirm that a kagome band structure is formed in the 2D MOF near the Fermi level. We demonstrate access to multiple molecular charge states in the 2D MOF using tip-induced local electric fields, which highlights the role of electron-electron interactions that are likely to give rise to exotic electronic properties. Furthermore, to realize the exciting prospect of truly designer materials, it is important to demonstrate MOF synthesis on other 2D substrates. Here, I will also discuss our recent efforts of synthesizing MOF on NbSe₂, which extends the synthesis and electronic tunability of 2D MOFs beyond the electronically less relevant metal and semiconducting surfaces to the superconducting substrates [5].

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Permeation through carbon nanomembranes

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Ultrathin carbon nanomembranes (CNMs), fabricated from crosslinking self-assemblies of molecular precursors, are 2D membranes that possess well-defined physical and chemical properties. With a simple transfer procedure, CNMs can be placed on various supports, enabling versatile applications. Here, we present the water and ion permeation characteristics of CNMs. CNMs with different precursor molecules and substrates are prepared and characterized by scanning probe microscopy. Varying molecules and coating conditions leads to the change in membrane morphology and thickness. Prepared from terphenylthiol (TPT) self-assembled monolayer on Au(111), CNMs have a thickness of 1.2 nm and a pore density of $\sim 10^{18} \text{ nm}^{-2}$. The high pore density allows a rapid water permeance of $1.1 \times 10^{-4} \text{ mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}\cdot\text{Pa}^{-1}$.¹ With the pore size $< 1 \text{ nm}$, TPT CNMs also show an extraordinarily high ion rejection, with a membrane resistance of $\sim 10^4 \Omega \text{ cm}^2$ in 1 M Cl^- solutions.² Combining these two properties, a forward osmosis experiment based on TPT CNM composites is demonstrated, highlighting their potentials in water filtration applications.

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Self-assembly behavior of molecules under confinement conditions

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Molecular self-assembly at solid surfaces is a rather complicated process involving different types of dynamics including adsorption and desorption.¹ Fundamental understanding is crucial to design the molecular structure and regulate the formation of self-assembled molecular networks (SAMNs).^{2,3} Here I will mainly focus on the self-assembly behavior of molecules under lateral confinement conditions on chemically modified highly oriented pyrolytic graphite (HOPG). Two types of molecule-based confinement conditions that require the chemical modification of the HOPG substrate will be introduced. The first type (“random confinement space”) is created by the spatially-random covalent attachment of aryl groups on HOPG. The second type (“nanocorrals or nanocontainers”) is the result of a nanolithography process, where pristine HOPG areas are formed by the local removal of the covalently attached aryl groups using the tip of a scanning tunneling microscope.

Upon dropcasting a quinonoid zwitterion derivative (QZ-C16) on top of the “random confinement space”, well-ordered domains could still be observed at and even below the threshold concentration, i.e. the concentration below which no self-assembly is observed on pristine graphite. The distinct self-assembly behavior on the modified surfaces provides an additional mechanistic understanding of molecular assembly at early stages. When the self-assembly of long alkanes is investigated in the “nanocontainers”, certain orientations of molecular domains are preferred, i.e. along the slow scanning axis to form inside the nanocorrals. As the alkyl chain length decreases though, this alignment effect becomes weaker.

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Exciton dynamics and electron delocalization in C₆₀ thin films

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The implementation of molecular materials in everyday technology is so far hindered by their poor charge carrier mobility compared to inorganic semiconductors. This low mobility is a direct consequence of the strong localization of the molecular valence and excited states on single molecular sites. Only in rare cases, delocalized valence states with strongly dispersive bands can be observed in molecular crystals. Here, we focus on such an exceptional case and study the band structure and excited states of C₆₀ thin films on Ag(111) and Cu(111). Using momentum microscopy, we find strongly dispersive valence bands with complex momentum-dependent photoemission patterns that point to the formation of an atomic crystal-like band structure in C₆₀ thin films [1]. Complementary, we explore the delocalization of the excited states of the fullerene thin films using time-resolved two-photon momentum microscopy. In our experiment, an ultrashort, fs light pulse optically excited the material system while a second, time-delayed UV pulse photoexcited the system thereby allowing us to follow temporal evolution of the photoemission patterns on a fs time-scale. We find three characteristic photoemission patterns in the excited state range that can be attributed to charge transfer and Frenkel-like excitons [3]. Characteristic differences in the time-dependent emission patterns for these three excited states (see e.g. Figure 1) can be correlated to the change in spatial extension of the excitonic wave function during transformation from high energy CT- into low energy Frenkel-like excitons.

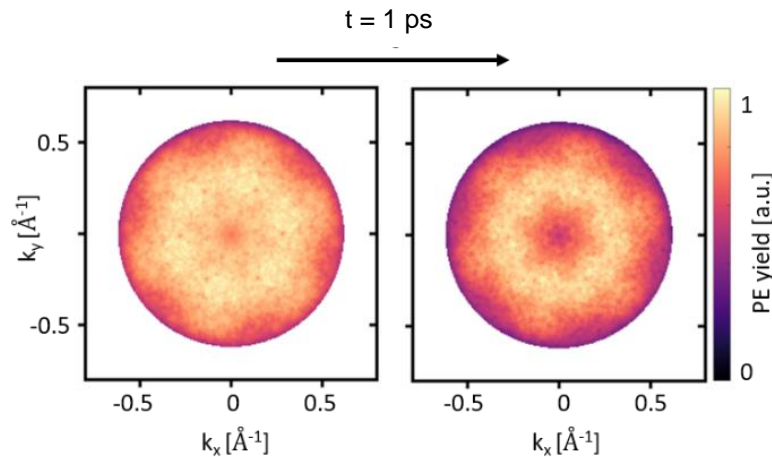


Figure 1. Temporal evolution at 0 ps (left) and 1 ps (right) delay of the CT₁ exciton of a C₆₀ thin film on Cu(111) measured with 2.95 eV pump and 5.9 eV probe laser pulses ($E - E_{\text{HOMO}} = 2.1$ eV).

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