# Functional Materials at Surfaces - Fabrication, Atomic-scale Characterization, and Advances Towards Application

## 809. WE-Heraeus-Seminar

**05 May – 10 May 2024**

**at the Physikzentrum Bad Honnef, Germany**

The WE-Heraeus Foundation supports research and education in science, especially in physics.
The Foundation is Germany’s most important private institution funding physics.

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 809. WE-Heraeus-Seminar:

The topic of functional materials at surfaces covers a wide range of material classes and length scales, from single surface-adsorbed organic molecules to extended 2D structures, and thus research areas. What these areas all have in common is the goal to understand the physics that ultimately defines the properties of these materials, and eventually to learn how to modify these properties in a controlled and reproducible manner to devise materials optimized for applications. One enormously powerful toolbox to achieve this is scanning probe microscopy (SPM). Over the past 40 years since its invention, SPM has evolved from a mere imaging technique to a tool that can provide information on structural, electronic, optical, and magnetic properties, and even facilitate the manipulation of individual adsorbates, all at the atomic level. These advances over the past decades have sparked tremendous progress not only in our understanding of the physics of such low-dimensional systems, but also in our ability to build structures with specifically tailored functionality. While the main focus of this seminar will be scanning probe based approaches, we want to also bridge the gap to alternative and complementary high-resolution characterization techniques.

This seminar, therefore, aims at providing an overview to some of the research areas within the rapidly growing fields of functional surface-adsorbed materials, covering recent progress in research on organic structures on surfaces, different deposition techniques, atomistic control of single molecules, as well as 2D materials beyond organic structures.

## Scientific Organizers:

| | |
|---|---|
| Dr. Katharina Kaiser | Universität Goettingen, Germany<br>E-mail: katharina.kaiser@uni-goettingen.de |
| Dr. Stefania Moro | University of Birmingham, UK<br>E-mail: s.moro@bham.ac.uk |
| Dr. Luis Parra López | Fritz Haber Institute of<br>the Max Planck Society, Germany<br>E-mail: lopez@fhi-berlin.mpg.de |

# Introduction

**Administrative Organization:**

| | |
|---|---|
| Dr. Stefan Jorda<br>Martina Albert | Wilhelm und Else Heraeus-Stiftung<br>Kurt-Blaum-Platz 1<br>63450 Hanau, Germany |

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**Venue:**

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**Registration:**

Martina Albert (WE-Heraeus Foundation)
at the Physikzentrum, reception office
Sunday (16:00 h – 20:00 h)
and Monday morning

# Program

# Program (CET)

## Sunday, 05 May 2024

| | | |
|---|---|---|
| 16:00 – 20:00 | **Registration** | |
| From 18:00 | *BUFFET SUPPER* | |
| 19:30 – 19:45 | Scientific Organizers | **Welcome and Opening** |
| 19:45 | Michael Crommie | **Controlling Electronic Filling in Molecular Assemblies** |

## Monday, 06 May 2024

| | | |
|---|---|---|
| 08:00 | *BREAKFAST* | |

| | | |
|---|---|---|
| 09:00 – 10:00 | Melanie Müller | **Advances in light-coupled STM: ultrafast dynamics and spectroscopy at atomic scales** |
| 10:00 – 10:45 | Sebastian Loth | **Ultrafast surface dynamics of 2D materials studied with THz-STM** |
| 10:45 – 11:15 | *COFFEE BREAK* | |
| 11:15 – 12:00 | Søren Ulstrup | **Visualizing field-tunable flat bands and many-body effects in twisted heterostructures with nanoARPES** |
| 12:00 – 12:45 | Marcel Reutzel | **Momentum microscopy & 2D materials: Excitons in space and time** |
| 12:45 | *LUNCH* | |

| | | |
|---|---|---|
| 14:00 – 15:00 | Gabriela Borin Barin | **Bottom-up graphene nanoribbons: from molecules to devices** |
| 15:00 – 15:45 | Martina Lihter | **Nanofabrication and functionalization of 2D materials for sensing and nanofluidic applications** |

# Program (CET)

## Monday, 06 May 2024

| | | |
|---|---|---|
| 15:45 – 16:15 | *COFFEE BREAK* | |
| 16:15 – 17:00 | Aran Garcia-Lekue | **Functional 1D and 2D molecular nanoarchitectures: insights from theory and simulations** |
| 17:00 – 17:45 | Alessandro Sala | **Multiscale characterization of functionalized 2D materials: from quantum confinement to embedding of foreign atoms** |
| 17:45 – 18:30 | Marc González Cuxart | **Growth and atomic-scale insights into 2D materials beyond graphene** |
| 18:30 – 19:45 | *DINNER* | |

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|---|---|
| 19:45 | **Meet the editor with Christian Kuttner (Nature Communications)** |

# Program (CET)

## Tuesday, 07 May 2024

| | | |
|---|---|---|
| 08:00 | *BREAKFAST* | |
| 09:00 – 10:00 | Shigeki Kawai | **Manipulation of single molecules and their structures** |
| 10:00 – 10:45 | Kwan Ho Au-Yeung | **A nanocar and rotor in one molecule** |
| 10:45 – 11:15 | *COFFEE BREAK* | |
| 11:15 – 12:00 | Florian Albrecht | **Selectivity in single-molecule reactions by tip-induced redox chemistry** |
| 12:00 – 12:45 | Grant Simpson | **Directional motion on surfaces investigated at the single-molecule scale** |
| 12:45 | *LUNCH* | |
| 14:00 – 15:00 | Alexander Weismann | **Tuning molecular magnetism and vibrational excitations by supramolecular manipulation** |
| 15:00 – 15:45 | **Poster flash** | |
| 15:45 – 16:15 | *COFFEE BREAK* | |
| 16:15 – 18:30 | **Poster session I** | |
| 18:30 | *DINNER* | |

# Program (CET)

## Wednesday, 08 May 2024

| | | |
|---|---|---|
| 08:00 | *BREAKFAST* | |
| 09:00 – 10:00 | Stephan Rauschenbach | **Atomic resolution molecular imaging based on soft-landing electrospray ion beam deposition** |
| 10:00 – 10:45 | Andreas Walz | **Soft-landing meets mass-spectrometry - gentle UHV deposition for large, reactive or fragile molecules to create functional nano-architectures** |
| 10:45 – 11:15 | *COFFEE BREAK* | |
| 11:15 – 12:00 | Kelvin Anggara | **Single molecule analysis of biomolecules by direct imaging** |
| 12:00 – 12:45 | Xiaocui Wu | **Imaging of conjugated polymers unveiling polymerization defects** |
| 12:45 | *LUNCH* | |
| 14:00 – 18:30 | **Excursion** | |
| 18:30 | *HERAEUS DINNER*<br>*(social event with cold & warm buffet and complimentary drinks)* | |

# Program (CET)

## Thursday, 09 May 2024

| | | |
|---|---|---|
| 08:00 | *BREAKFAST* | |
| 09:00 – 10:00 | Mikhail Fonin | **Electrospray deposition and on-surface investigation of single molecule magnets** |
| 10:00 – 10:45 | Rémy Pawlak | **Giant thermal expansion of a two-dimensional supramolecular network triggered by alkyl chain** |
| 10:45 – 11:15 | *COFFEE BREAK* | |
| 11:15 – 12:00 | Lukas Grossmann | **Mesoscale ordered 2D polymers by on-surface photopolymerization – The substrate influence** |
| 12:00 – 12:45 | Sabine Maier | **On-surface synthesis: a bottom-up strategy to atomically precise nanographenes** |
| 12:45 | *LUNCH* | |
| 14:00 – 15:00 | Meike Stöhr | **Metal-organic and covalently bonded nanostructures on metals and graphene** |
| 15:00 – 15:45 | **Poster flash** | |
| 15:45 – 16:15 | *COFFEE BREAK* | |
| 16:15 – 18:30 | **Poster session II** | |

# Program (CET)

## Friday, 10 May 2024

| | | |
|---|---|---|
| 08:00 | *BREAKFAST* | |
| 09:00 – 10:00 | Erik Vesselli | **Ligation and molecular activation at 2D biomimetic functional materials. A surface science perspective** |
| 10:00 – 10:45 | Elizabeth Boer-Duchemin | **Local electrical excitation of excitons in 2D semiconductors** |
| 10:45 – 11:15 | *COFFEE BREAK* | |
| 11:15 – 12:00 | Markus Huber | **Ultrafast terahertz nanoscopy of quantum materials** |
| 12:00 – 12:45 | Scientific organizers | **Poster Prize Awards & Closing Remarks** |
| 12:45 | *LUNCH* | |

**End of the seminar and departure**

# Posters

# Posters I

| | |
|---|---|
| Humaira Akber | **Unveiling Periodicities: Nonreciprocal CDW Proximity Effects in Monolayer NbSe2/TiSe2 Heterojunctions** |
| Paula Angulo Portugal | **Assisted on-surface synthesis of porous graphene nanoribbons on vicinal surfaces** |
| Arnab Banerjee | **Controlling Yu-Shiba-Rusinov States in Supramolecular arrays using Molecular Switches** |
| Michele Capra | **Growth and characterization of sharp, atomically flat graphene/oxide heterojunctions** |
| Joel Deyerling | **On-Surface Synthesis of Peripherally Oxygen-Annulated Porphyrins** |
| Xabier Diaz de Cerio | **Tuning quantum electronic transport and anisotropy in nanoporous graphene** |
| Abdelhadi El Hachmi | **Investigation of structural and magnetic properties of ceramics Sr3Fe2+xMo1−xO9−3x/2 (x = 0.45, 0.60, and 1)** |
| Filippo Giovanni Fabozzi | **Voltage-Gated Reversible Switching of Moiré Patterns in Organic Two-Dimensional Molecular Crystals** |
| Ilias Gazizullin | **On-surface reactions of triazido-s-heptazine** |
| Thiago Gonzales-Llana Brito | **Investigating the Role of ITO Substrate and Sample Condition in Electronic and Optical Properties of WSe2 Monolayers** |
| Max Halbauer | **Measuring and Mapping Elongation of Single Helicene Molecules by NC-AFM** |

# Posters I

| | |
|---|---|
| Stefanie Hilgers | **Exploring the structural and chemical composition of antimony monolayer on Ag(110)** |
| David Janas | **Probing molecular conformation via photoemission orbital tomography** |
| Alejandro Jiménez-Martin | **Coverage-modulated halogen bond geometry transformation in supramolecular assemblies** |
| Natasha Khera | **Adsorption Behavior of N Heterocyclic Carbene with Thiophene on Au(111)** |
| Dhaneesh Kumar Gopalakrishnan | **Unravelling Glycan Structures: ESIBD+STM Exploration of Stapled Conformations** |
| Paul Laubrock | **Single molecule manipulation for Scanning Quantum Dot Microscopy tip functionalization** |

# Posters II

| | |
|---|---|
| Xuanchen Li | **Bottom-up Fabrication and Scanning Probe Microscopy Characterization of Graphene Nanoribbons** |
| Leonard-Alexander Lieske | **Distance-Dependence of Orbital Density Imaging Using a CO-Functionalized (p-wave) STM Tip** |
| Huang Longfeng | **Reactivity of single metal atoms in different coordination environments** |
| Felix Lüpke | **Engineered quantum states in assembled van der Waals heterostructures** |
| Marta Macyk | **Unraveling the influence of ferroelectricity on oxide perovskite surfaces and their photocatalytic reactions** |
| Paola Mantegazza | **Detailed structural information of conjugated polymers revealed by high resolution scanning tunnelling microscopy** |
| Florian Münster | **Electrospray Ionization Ion Beam Deposition of Organic Molecules** |
| Tim Naumann | **Nitrogen-Doped Carbon Nanostructures by Combined In-Solution and On-Surface Chemistry** |
| Abdallah Nayad | **Towards the isolation of silicene quantum dots from chemical exfoliation** |
| Oussama Oulhakem | **Effect of water intercalation into tungsten trioxide structure (WO3.xH2O) (x=0,1,2): Correlation between structure and photocatalytic performance** |

# Posters II

| | |
|---|---|
| Grigori Pasko | **Synthesis and Characterization of Pentadecacene (15ac) by Tip-manipulation with a Scanning Probe Microscope** |
| Sergio Salaverria Bugallo | **On-surface synthesis and characterization of [19]-starphene** |
| Matthew Timm | **How to measure cones of reaction for single-molecule collisions** |
| Birce Sena Tömekce | **Borazine-doped Carbon Scaffolds: From Single Molecules to 2D-BNC Architectures** |
| Henrik Wiedenhaupt | **STM Luminescence of Ultrathin ZnO Films on Ag(111)** |
| Alfonso Yubero-Navarro | **On-surface molecular sensors for individual Ba tagging: application in neutrinoless double beta decay experiments** |
| Kassandra Zoltner | **On Surface synthesis of a Dicaesium Tetraphenylporphyrin Complex** |

# Abstracts of Lectures

(in alphabetical order)

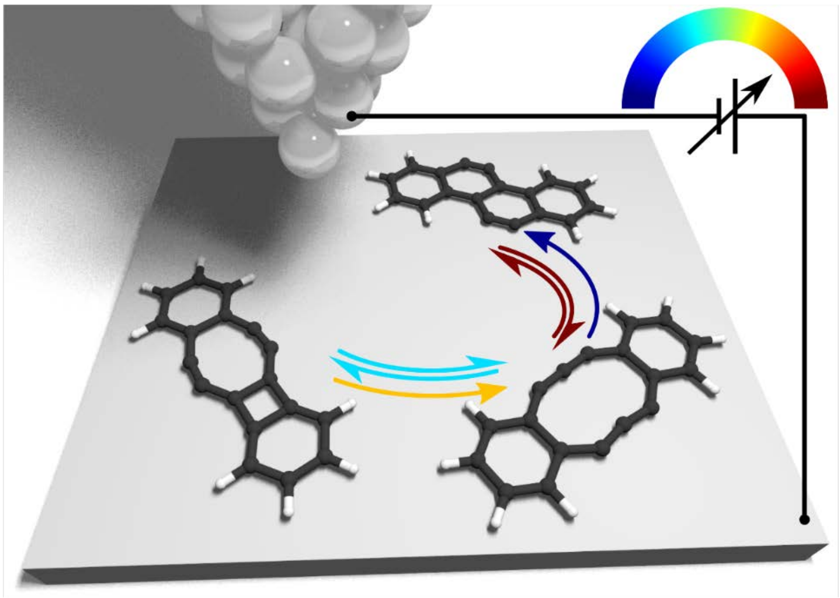
# Selectivity in single-molecule reactions by tip-induced redox chemistry

**Florian Albrecht**[1], Shadi Fatayer[1,2], Iago Pozo[3], Ivano Tavernelli[1], Jascha Repp[4], Diego Peña[3], Leo Gross[1]

*[1] IBM Research Europe — Zurich, Rüschlikon, Switzerland*
*[2] Physical Science and Engineering Division, King Abdullah University of Science and Technology (KAUST), Thuwal, Saudi Arabia*
*[3] Centro Singular de Investigación en Química Biolóxica e MateriaisMoleculares (CiQUS) and Departamento de Química Orgµnica, Universidade de Santiago de Compostela, Santiago de Compostela, Spain*
*[4] Institute of Experimental and Applied Physics, University of Regensburg, Regensburg, Germany*

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

[1] S.-W. Hla et al., *Phys. Rev. Lett*. **85**, 2777 (2000)
[2] F. Albrecht et al., *Science* **377**, 298 (2022)



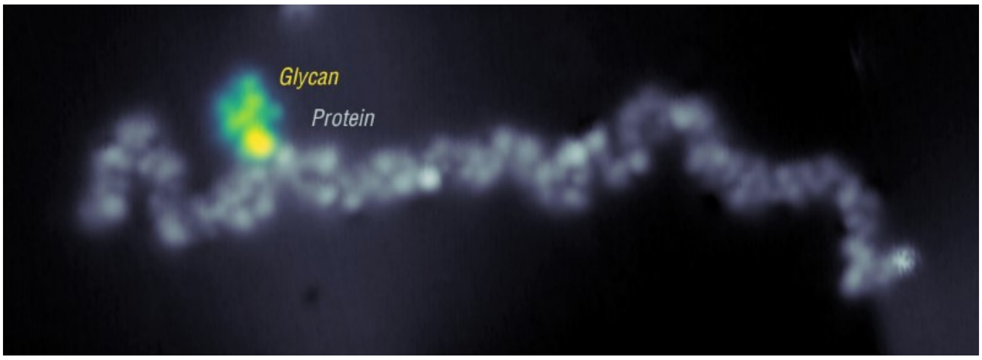
# Single molecule analysis of biomolecules by direct imaging

**Kelvin Anggara**

*Max Planck Institute for Solid State Research, Stuttgart, Germany*

Diverse structures of biomolecules in living systems pose challenges for present analytical methods in analyzing their individual structures. Ensemble-averaged measurement on molecules with extensive variation causes loss of structural information for individual molecules. Here we overcome this problem by imaging and analyzing single biomolecules deposited intact on surfaces.

Biomolecules were transferred to the gas-phase by electrospray, mass-selected, and soft-landed at a metal surface, using the Electrospray Ion Beam Deposition (ESIBD) technique – and imaged one-at-a-time by Scanning Tunneling Microscopy (STM) corroborated by DFT calculations. We have successfully applied our approach to glycans [1-4] as well as lipids and proteins decorated with glycans [5], whose analyses remain intractable by current methods. Our approach presents a means to access individual structures of any biomolecules that can be electrosprayed and deposited onto a surface.



False color STM image of a glycan-decorated protein reveals the attachment site and structure of the glycan on the protein. Adapted from Ref [5].

## References

[1] X. Wu, *et. al.* Imaging Single Glycans. *Nature* **582**, 375 (2020).

[2] K. Anggara, *et. al.* Exploring the Molecular Conformation Space by Soft Molecule-Surface Collision. *JACS* **142**, 21420 (2020).

[3] K. Anggara, *et. al.* Identifying the Origin of Local Flexibility in a Carbohydrate Polymer. *PNAS* **113**, e2102168118 (2021).

[4] J. Seibel, *et. al.* Visualizing Chiral Interactions in Carbohydrates Adsorbed on Au(111) by High-Resolution STM Imaging. *Angew. Chem.* **62**, e202305733 (2023).

[5] K. Anggara, *et. al.* Direct Observation of Glycans bonded to Proteins and Lipids at the Single Molecule Level. *Science* **382**, 219 (2023).

# A Nanocar and Rotor in One Molecule

**K. H. Au-Yeung[1±], S. Sarkar[1], O. Aiboudi[2], D. A. Ryndyk[3, 4], R. Robles[5, 6], N. Lorente[5, 6], F. Lissel[2], C. Joachim[7], F. Moresco[1]**

[1] *Center for Advancing Electronics Dresden, TU Dresden, 01062 Dresden, Germany*
[2] *Leibniz-Institut für Polymerforschung Dresden e.V., 01069 Dresden, Germany, and Faculty of Chemistry and Food Chemistry, TU Dresden, 01062 Dresden, Germany*
[3] *Institute for Materials Science, TU Dresden, 01062 Dresden, Germany*
[4] *Theoretical Chemistry, TU Dresden, 01062 Dresden, Germany*
[5] *Centro de Física de Materiales CFM/MPC (CSIC-UPV/EHU), 20018 Donostia-San Sebastián, Spain*
[6] *Donostia international physics center, 20018 Donostia-San Sebastian, Spain*
[7] *GNS & MANA Satellite, CEMES, CNRS, 29 rue J. Marvig, 31055 Toulouse, France*

Achieving precise control over the semi-classical mechanical movements of single molecules paves the way for generating useful work at the nanoscale. Inspired by macroscopic machines, examples of molecule-gears, rotors/motors, and nano-vehicles (Nanocar) adsorbed on surfaces have been demonstrated recently. However, they are often driven by completely different and sometimes not completely understood mechanisms.

In this talk, we will focus on the dual functionality of a zwitterionic single molecule machine on a Au(111) surface by low-temperature STM. We will show how this molecule can act as a unidirectional single-molecule rotor when chemically anchored, and a fast-drivable nanocar when physisorbed. By adjusting molecular coverage, we selectively tune its conformation as a rotor or a nanocar. Investigating the microscopic reversibility principle, we delve into the interplay between thermal and electron tunneling excitations for the unidirectional rotation of the rotors. We identify a range of moderate voltages and temperatures that enhances the one-way rotational rates. Under voltage pulses in the STM junction, the rotation is predominantly influenced by electron tunneling, while elevated temperatures become stochastic.

## References

[1] K. H. Au-Yeung et al. ACS Nano **17**, 3, 3128–3134 (2023)
[2] K. H. Au-Yeung et al. J. Phys. Chem. C **127**, 34, 16989–16994 (2023)

[±] *Current Address: Physikalisches Institut, Karlsruhe Institute of Technology, 76131 Karlsruhe*

# Local Electrical Excitation of Excitons in 2D Semiconductors

**Elizabeth Boer-Duchemin**

*Institut des Sciences Moléculaires d’Orsay (ISMO),*
*Université Paris-Saclay, Orsay, France*

We use a biased tunnelling junction to locally and electrically excite excitons in two-dimensional semiconductors. The tunnelling junction that is used is the one found between the tip of a scanning tunnelling microscope (STM) and a conducting substrate on which we have deposited a monolayer of a transition metal dichalcogenide (TMD) material[1-3]. Our setup combines ambient scanning probe microscopy (STM/AFM) with an inverted optical microscope, leading to wide-field imaging capabilities. More precisely, thanks to real plane imaging, we can determine where on the sample the collected light is emitted from, while through Fourier plane analysis the emission angle of the light is known, thus providing a powerful tool for the interpretation of the physical phenomena at play. Thanks to this technique we have studied exciton diffusion, the orientation of the transition dipole moments, and the controlled quenching of luminescence.

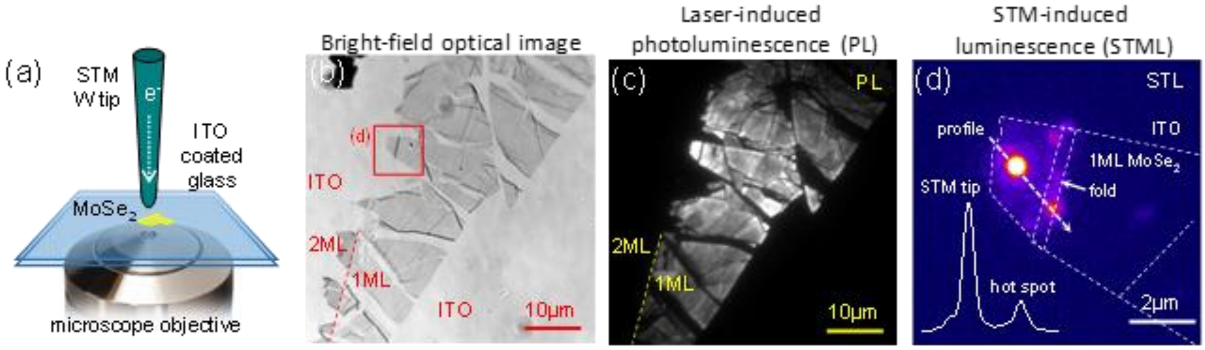


Figure 1: STM-induced generation of excitons in 2D semiconductors. a) Experiment: tunnelling current flows between the tungsten STM tip and the biased sample, which is a mechanically exfoliated $MoSe_2$ flake on ITO on glass. b) Monolayer and bilayer regions are identified with difficulty using transmission optical microscopy. c) Monolayer and bilayer regions are easily identified using laser-induced photoluminescence. d) STM luminescence is induced locally; the bright spot in the image at the tip location demonstrates that most of the created excitons recombine close to the excitation position. Note that others diffuse in the flake and recombine at a “hot spot”.

[1] D. Pommier et al., Phys. Rev. Lett., **123**, 027402 (2019)
[2] R. J. Peña Román et al., Phys. Rev. B, **106**, 085419 (2022)
[3] R. J. Peña Román et al., Nano Letters **22**, 9244 (2022)

# Bottom-up graphene nanoribbons: from molecules to devices

Gabriela Borin Barin

nanotech@surfaces Laboratory, Empa, Dübendorf, Switzerland

Graphene nanoribbons (GNRs) show exciting properties deriving from electron confinement and related band gap tunability[1]. The ability to tune GNRs' electronic and magnetic properties at the single atom level makes them an ideal platform for a wide range of device applications, from classical transistors to spintronics. In this talk, I will overview the necessary steps to bring GNRs from ultra-high vacuum (UHV) to device integration, focusing on the main aspects of synthesis, characterization, and transport measurements of atomically precise graphene nanoribbons. After the UHV bottom-up synthesis, GNRs are transferred using different transfer methods based on wet[2] and semi-dry/dry-transfer methods. Those processes allow the characterization of GNRs fingerprint modes via Raman spectroscopy[3] and the characterization of their electronic properties on decoupled substrates such as quasi-free-standing graphene on SiC. Next, I will show our progress in integrating different armchair GNRs (5-, 9-, 17-AGNRs) into field-effect transistors with different gate and contact configurations. We demonstrated the highest $I_{on}$ current GNR-FET device to date by using a double-gate configuration[4]. 9-AGNR-FETs showed $I_{on}$ currents up to 12μA and $I_{on}/I_{off}$ up to $10^5$. By integrating 9-AGNRs into FET devices using graphene and carbon nanotubes[5] as electrodes, we also reported tunable multi-gate devices showing quantum dot behavior with rich Coulomb diamond patterns, Figure 1.

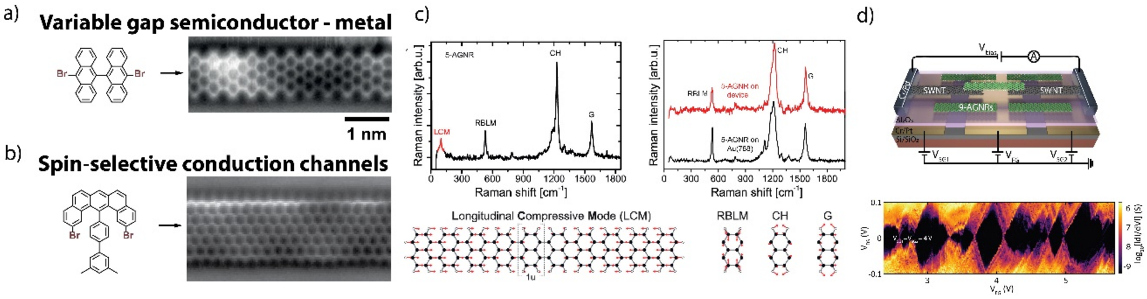


**Figure 1:** a) and b) *precursor monomers for GNRs with different edge topology and correspondent noncontact atomic force microscopy (nc-AFM) images, c) Raman spectrum of 5-AGNRs with the assignment of the most prominent peaks on Au (111) and on the device substrate after transfer; atomic displacement profiles obtained from DFT calculations of 5-AGNRs, d)* Schematic of the device, using CNT as electrodes, including the measurement circuit; stability diagram showing single-electron charging behaviour.

[1] J. Cai *et al.*, Nature, **466**, 2010
[2] G. Borin Barin *et al*., ACS Applied Nanomaterials, **2**, 2019
[3] R. Darawish *et al*, Carbon, 2018, 2024
[4] Z. Mutlu *et al.*, IEEE International Electron Devices Meeting (IEDM), 37.4. 1-37.4. 4, 2021
[5] J. Zhang *et al, Nature Electronics, 6, 2023*

# Controlling Electronic Filling in Molecular Assemblies

Michael F. Crommie
UC Berkeley Physics Department, UC Berkeley, Berkeley, CA, USA
Materials Sciences Division, LBNL, Berkeley, CA, USA

Electrically doping 2D molecular assemblies remains a significant challenge. Most molecular materials are made from closed-shell precursors that result in filled electronic bands with no free charge or spin. Charge-doping techniques common in other material classes, such as impurity doping and electrostatic gating, are still in their infancy for surface-assembled molecular systems. I will discuss two different physical systems where we have made some progress toward creating molecular assemblies where charge and spin are not locked up in filled bands. The first system involves metal-organic networks of N-heterocyclic carbenes. Here metal atoms bridge carbene centers and provide one extra electron per unit cell, thus facilitating the creation of partially-filled bands. We have successfully fabricated 1D and 2D carbene networks and imaged them using scanning tunneling microscopy (STM). These result in low work function materials with strong charge transfer characteristics. The second system that I will discuss involves high-electron-affinity molecules ($F_4$TCNQ) combined with graphene single-layer field-effect transistors (FETs). Electrostatically gating such molecules at the surface of FETs enables their charge state to be switched, thereby altering the interaction between molecules and inducing them to assemble into different gate-tunable collective phases that can be imaged by STM. At low charge-carrier density the molecules undergo a reversible transition between a charge-neutral van der Waals “ice” and an ionic liquid phase. At high charge-carrier density we find evidence for a molecular hexatic phase having long-range orientational order. Prospects for observing the transition to molecular Wigner crystal phase at even higher charge-carrier density will be discussed.

# Electrospray Deposition and On-Surface Investigation of Single Molecule Magnets

**F. Paschke[1], T. Birk[1], Ph. Erler[1], and M. Fonin[1]**

[1]*Department of physics, University of Konstanz, 78467 Konstanz, Germany*

The controlled deposition, characterization and manipulation of single molecule magnets (SMMs) on surfaces is one of the crucial points to be addressed with regard to their possible implementation as functional units in future electronic and spintronic devices. Profound understanding of molecule-molecule and molecule-substrate interactions is required as well as unraveling their effect on the molecular electronic and magnetic properties. Local measurement techniques like scanning tunneling microscopy (STM) together with ensemble-averaging methods like X-ray absorption spectroscopy (XAS) have been proven to set up an appropriate frame to study these materials. The majority of these studies deal with SMMs that exhibit rather simple structures with mostly only one magnetic ion. The situation becomes more complicated when it comes to larger polynuclear compounds that can be quite fragile with respect to the surface deposition or not easy to organize on surfaces due to their bulky ligand shell. Here, we provide an overview of our results on successful deposition of polynuclear SMMs on functional surfaces by employing the electrospray deposition (ESD) method. We will briefly focus on ESD implementation in our home laboratory and further discuss several examples of surface-deposited SMMs. In particular, our investigations on $Fe_4H$ [1] and $Dy_2@C_{80}(CH_2Ph)$ [2] will be presented.

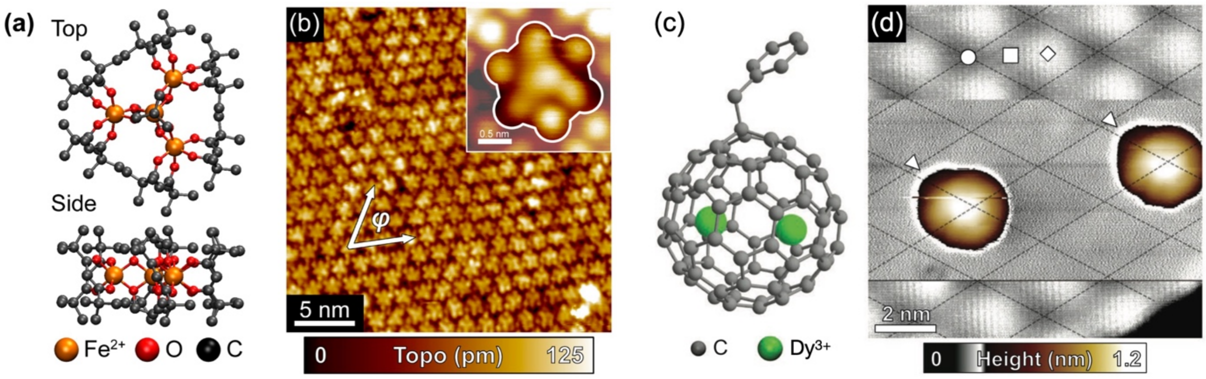


**Figure 1.** (a) Molecular structure of $Fe_4H$. (b) STM images of $Fe_4H$ on Au(111) with the direction of the unit cell vectors sketched in white. Inset: Magnified image of a single molecule with its 3-fold symmetry. (c) Molecular structure of $Dy_2@C_{80}(CH_2Ph)$. (d) STM topographic image of two isolated molecules on the graphene/Ir(111) surface. White triangles denote the protruding side group.

## References

[1] L. Gragnaniello *et al.*, Nano Lett. **17**, 7177 (2017).
[2] F. Paschke *et al.*, Small **18**, 2105667 (2022).

# Functional 1D and 2D molecular nanoarchitectures: insights from theory and simulations

**Aran Garcia-Lekue**[1,2]

[1]*Donostia International Physics Center (DIPC), Donostia-San Sebastián, Spain*
[2] *Ikerbasque, Basque Foundation for Science, Bilbao, Spain*

Nanostructuring graphene with atomic precision is now possible by on-surface synthesis methods,[1,2] which has boosted the research attempts to create novel 1D and 2D carbon-based nanostructures attractive for electronic, spintronic or quantum applications. In tandem with the experimental advances, theory and simulation has become an essential partner in order to achieve an atomic level understanding and control of their properties.

In this talk, I will present some studies of prototype graphene nanostructures, such as graphene nanoribbons (GNRs) and nanoporous graphene (NPG), that we have recently performed in our group. Combining density functional theory (DFT), tight-binding (TB) models and non-equilibrium Green's functions (NEGF) approach, and in collaboration with our experimental colleagues, we have investigated their electronic, magnetic and transport properties. On the one hand, we have explored the emergence of localized spins in GNRs realized by substitutionally doping GNR with boron atoms in its interior.[3] We have also reported on the highly tunable electron propagation on a novel NPG structure.[4] From a purely theoretical perspective, we have investigated prototypical hybrid GNRs formed by mixing carbon-based precursor molecules and porphyrin centers, as well as bilayers composed of NPG and graphene.[5,6]

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# Growth and atomic-scale insights into 2D materials beyond graphene

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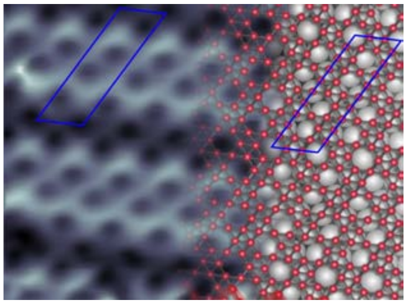
Inspired by the early example of graphene, most two-dimensional (2D) materials developed in the following years have been isolated from naturally occurring layered materials. This approach, however, restricts the library of attainable materials. Synthetic growth methods can overcome this limitation by allowing custom choice of constituent elements, hence unlocking vast new possibilities for creating 2D materials with tailored properties. Borophenes, consisting on atomically-thin layers of elemental boron, are prominent examples of synthetic 2D materials, as they exhibit anisotropic metallicity and mechanical properties that expand the capabilities of conventional 2D materials [1]. Their intriguing multicenter boron-boron bonding results in the formation of a large number of 2D polymorphs (i.e., borophenes). These are typically grown on epitaxial substrates, in which interfacial interactions strongly influence the stabilization of a particular polymorph. It is therefore crucial to gain atomic-scale insights into these materials and explore suitable synthesis process for properties tailoring and creation of functional borophene-based heterostructures.

In this talk, I will first review the exploration of borophenes since the early computational attempts to stabilize 2D boron structures, to the most recent advances towards device incorporation. Next, I will present how to grow borophenes by chemical vapor deposition, and the versatility of this method to fabricate functional borophene – hexagonal boron nitride heterostructures [2]. Atomic-scale insight into their structural, electronic and chemical properties is achieved thanks to a correlative study making use of scanning tunneling microscopy and synchrotron-based x-ray photoelectron spectroscopies [3]. Finally, I will assess whether the anisotropic structures of borophenes can be used as a unidirectional nano-template to steer molecular self-assembly, and compare it to the case of one-dimensionally corrugated hexagonal boron nitride [4]. These findings represent a step forward in the investigation these fascinating 2D materials, and exemplify the power of combining local-scale scanning probe microscopies with surface-averaged spectroscopic techniques.



*Borophene $X_6$ polymorph on an Ir(111) surface imaged by scanning tunneling microscopy*

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# Mesoscale Ordered 2D Polymers by On-Surface Photopolymerization – The Substrate Influence

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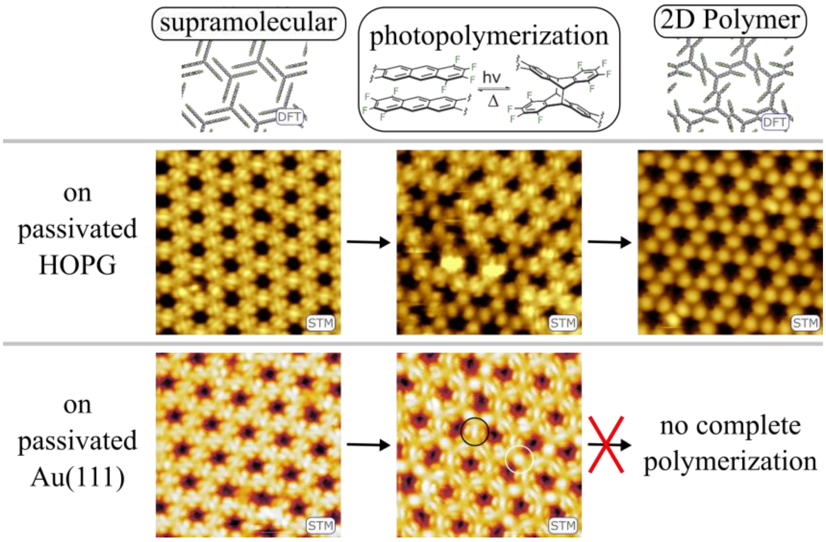
We synthesized mesoscale-ordered 2D Polymers by a topochemical on-surface photopolymerization using a fluorinated anthracene triptycene (fantrip) monomer.
Formation of the suitable supramolecular structure is the first essential step. Although fantrip is designed to self-assemble into a photoactive arrangement, it was still necessary to passivate the used substrates with either alkane (on graphite) or iodine (on Au(111) / Ag(111)) monolayers. In the second step, illumination with laser light (λ = 405 nm) excites the formation of intermolecular covalent bonds by a [4+4] cycloaddition. This photopolymerization process produces a 2D polymer that is topologically identical to the self-assembly and therefore maintains its long-range order. Moreover, the crosslinking increases the HOMO-LUMO gap, leading to pronounced differences in the STM contrast between reacted and unreacted linkages. This allowed us to study the time course of the polymerization by consecutive illumination.
While fantrip self-assembly on both passivated graphite and Au(111)/Ag(111) appears similar, significant differences were observed with regard to the photopolymerization. These effects may be attributed to the combined action of quenching and photoexcitation through the substrate, as well as the substrate's dielectric properties and possible registry effects.



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# Ultrafast terahertz nanoscopy of quantum materials

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Pushing optical microscopy to the shortest length- and timescales has been a key prerequisite to establish a causal link between nanoscopic elementary dynamics and macroscopic functionalities of matter. In this talk, I will show two recent breakthroughs in understanding and tracing ultrafast nanoscale dynamics in condensed matter systems.

First, I will discuss how ultrafast terahertz nanoscopy unravels the interplay between single-grain structure, composition and carrier dynamics in lead halide perovskite films [1] – a promising class for future solar cell devices. Phonon fingerprinting allows us to discern nano-grains of different crystallographic phase and chemical composition via the local dielectric function extracted from our experimental data. Tracing the carrier dynamics that follow photoexcitation with an optical pump pulse, we push the technique to extreme temporal resolution. By accessing deep-subcycle shifts of the detected terahertz near-field waveforms, we develop an approach to access the out-of-plane charge carrier diffusion – a key quantity for solar cell performance. A surprising robustness of diffusion against structural and chemical variations is found on the nanoscale, possibly shedding light on the origin of the remarkable performance of perovskite-based devices. Our approach may help resolve further unanswered questions, including the details of the charge collection process at the extraction layers or the impact of hot carrier effects.

Secondly, I will present a fundamentally new approach which brings all-optical microscopy to the atomic scale while retaining subcycle temporal resolution for the first time [2] based on extreme nonlinearities within tip-confined evanescent light fields. We demonstrate the capabilities of this new “Near-field Optical Tunnelling Emission” (NOTE) microscope by imaging packing defects on the surface of gold, alongside tracing the subcycle flow of electrons between the scanning tip and a semiconducting van der Waals trilayer in real-time. NOTE microscopy is not only compatible with insulating samples, where no large-scale currents can flow but also enables us to combine all-optical subcycle spectroscopy with atomic resolution. By doing so, NOTE provides direct access to atomic scale quantum light-matter interaction and dynamics on their intrinsic length and timescales.

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# Manipulation of single molecules and their structures

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Since the invention of scanning tunnelling microscopy and atomic force microscopy, manipulation of single atom and molecule has attracted tremendous interests of researcher. Particularly, combining with bond-resolved scanning probe microscopy,[1] this field has been rapidly developed. We can now control not only the position of the single molecules [2] but also their structures [3]. The structure of the small molecule is first identified by imaging, and then is modified by tunneling current/force. The position and the structure are finally identified by imaging again.

Here, we present our recent activities on tip-induced manipulations of single molecules with low-temperature scanning probe microscopy. We employed on-surface syntheses to obtain several compounds. For instance, dehydroazulene isomer and diradical units in three-dimensional organometallic compounds were obtained on Ag(111) and Au(111).[4] Tip-induced voltage pulses firstly resulted in the formation of a diradical species via successive homolytic fission of two C-Br bonds in the naphthyl groups, which are subsequently transformed to chiral dehydroazulene moieties. The delicate balance of the reaction rates among the diradical and two stereoisomers, arising from an in-line configuration of tip and molecular unit, allowed directional azulene-to-azulene and azulene-to-diradical local probe isomerization in a controlled manner (Figure). We further investigated the spin coupling in the diradical unit.

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# Nanofabrication and functionalization of 2D materials for sensing and nanofluidic applications

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Two-dimensional (2D) materials exhibit unique electronic, optical, and mechanical properties, making them highly versatile building blocks for various applications in (opto)electronics, catalysis, sensing and biosensing, energy harvesting etc. Incorporating these materials into nanoscale devices, such as nanopore-based nanofluidic systems and field-effect transistors (FETs), opens extensive opportunities, especially in biosensing and the manipulation of molecules and ions at the single-molecule level. This talk will focus on nanofabrication and applications of nanopores[1,2] and nanopore-FET[3] devices fabricated from 2D materials, including approaches for chemically modifying them[4,5] to create novel hybrid materials and tailor their properties for specific applications.

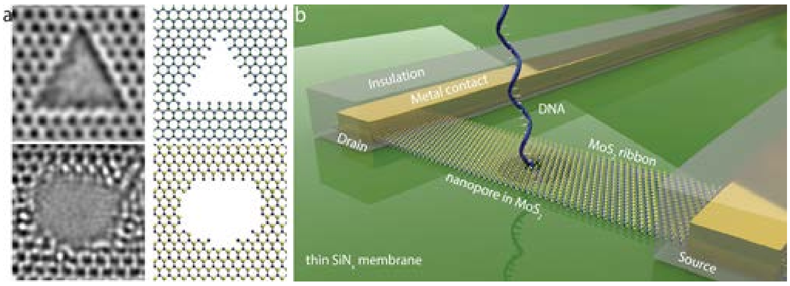

Figure 1 (a) HR-TEM images of nanopores in hexagonal boron-nitride (top) and MoS2 (bottom). (b) An illustration of a nanopore-FET device. Adapted from [2] and [3].

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# Ultrafast surface dynamics of 2D materials studied with THz-STM

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The intricate interplay between electrons and phonons significantly influences the behavior and properties of materials. Understanding the dynamics of these fundamental processes at the nanometer length scale and ultrafast time scale is essential for advancing our knowledge of collective excitations, emergence of correlated states and electronic phase transitions. Combining scanning tunneling microscopy (STM) with ultrafast pump-probe spectroscopy enables experiments that achieve such extreme temporal and spatial resolution in one experiment [1,2].
We make use of the extreme field enhancement at the apex of an STM tip to excite surfaces locally with single-cycle terahertz (THz) light pulses [3]. The tip-enhanced electric field can excite phonons [4] and collective charge excitations [5] directly under the STM tip, enabling the recording of ultrafast movies of surface dynamics at femtosecond speeds.

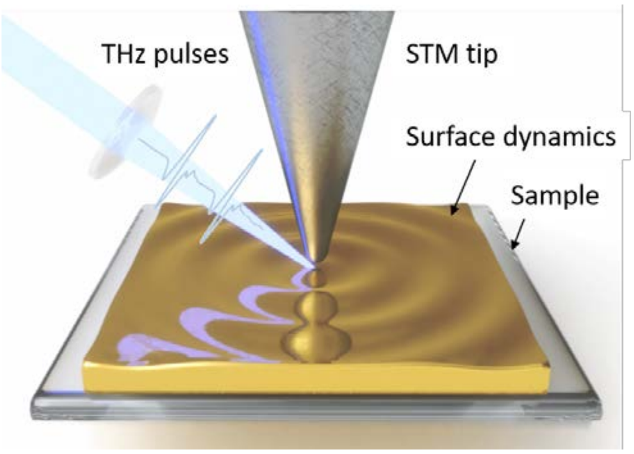

**Figure 1**. A scanning tunneling microscope (STM) can measure ultrafast surface dynamics on a sample when the tunnel junction is excited by pairs of THz pulses: one pulse excites the dynamics and the other probes them in a stroboscopic fashion by THz-induced tunneling of electrons.

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# ON-SURFACE SYNTHESIS: A BOTTOM-UP STRATEGY TO ATOMICALLY PRECISE NANOGRAPHENES

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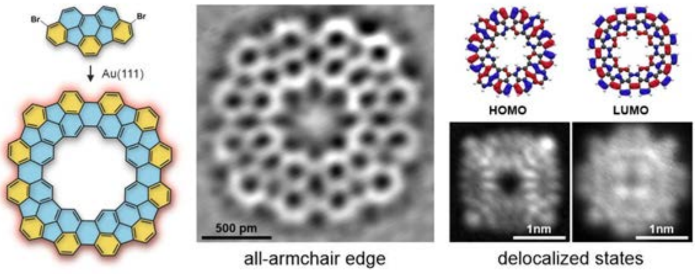
On-surface synthesis via covalent coupling of adsorbed molecules on metal surfaces has gained significant interest. This approach enables the creation of low-dimensional carbon materials with atomic-level precision, showcasing unique properties that are closely linked to their structure. To understand and control the surface-chemistry-driven synthesis, many efforts have been made to design smart precursors, explore novel reaction schemes, and utilize templating effects from the substrate.

My presentation focuses on high-resolution scanning probe microscopy experiments combined with density functional theory to demonstrate recent highlights on the assembly and characterization of physical properties of surface-supported low-dimensional molecular structures. [1-3] First, the assembly and electronic structure of planar π-extended cycloparaphenylene macrocycles, which represent the first nanographene with an all-armchair edge topology, will be discussed.[4] In the second part, I will outline the assembly and electronic properties of bowl-shaped nanographenes with a porphyrin core, so-called graphyrines, that exhibit a bowl-to-dome inversion.[5]



Planar π-extended cycloparaphenylene synthesized by on-surface [1]

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# Advances in light-coupled STM: Ultrafast dynamics and spectroscopy at atomic scales

**M. Müller**[1]

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Recent advances in the efficient coupling of optical and Terahertz (THz) electromagnetic radiation with low-temperature scanning tunneling microscopes (STM) have greatly expanded the possibilities for studying the properties and dynamics of excited states and non-equilibrium processes on surfaces. A number of technical developments have enabled the combination of atomically sharp STM tips with standard far-field optical spectroscopy and pump-probe approaches, bringing established laboratory optical and ultrafast techniques down to the atomic scale.

On the one hand, the realization of atomically stable plasmonic nanocavities in STM allows the confinement of light to subnanometer scales [1], enabling the mapping of luminescence and Raman spectra or the generation of photocurrents with unprecedented precision, thus allowing the study of excited states with simultaneous angstrom spatial and sub-meV energy resolution. On the other hand, new pump-probe schemes and well-defined junction excitation using modern ultrafast lasers and broadband THz pulses have revolutionized the capabilities of ultrafast STM (USTM) to study coherent vibrational dynamics and electronic excitations at surfaces with femtosecond temporal resolution [2], providing real-time access to non-equilibrium ultrafast dynamics at the angstrom scale.

In this talk I will give an overview of the achievements and developments that the field of light-coupled and ultrafast STM has experienced in recent years. In particular, I will discuss current and future applications of USTM for the study of ultrafast electronic and structural dynamics at solid surfaces and in quantum materials [2]. I will present recent work in which we use all-optical photon-driven [3] as well as THz-lightwave-driven STM (THz-STM) [4] to study coherent phonon dynamics locally at the (sub-)nanoscale, and will discuss the ability of THz-STM to probe and image photoexcited dynamics on time scales much faster than a single THz cycle [4].

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# Giant thermal expansion of a two-dimensional supramolecular network triggered by alkyl chain

**R. Pawlak,** **S. Scherb, J.G. Vilhena, A. Hinaut and E. Meyer**

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Thermal expansion, the response in shape, area or volume of a solid with heat, is usually large in molecular materials compared to their inorganic counterparts. Resulting from the intrinsic molecule flexibility, conformational changes or variable intermolecular interactions, the exact interplay between these mechanisms is however poorly understood down to the molecular level. We investigate the structural variations of a two-dimensional supramolecular network spray-deposited [1] on Au(111) consisting of shape persistent polyphenylene molecules equipped with peripheral dodecyl chains. By comparing high-resolution scanning probe microscopy and molecular dynamics simulations obtained at 5 and 300 K, we determine the thermal expansion coefficient of the assembly of $980 \pm 110 \times 10^{-6}\,\mathrm{K}^{-1}$, twice larger than other molecular systems hitherto reported in the literature, and two orders of magnitude larger than conventional materials. This giant positive expansion originates from the increased mobility of the dodecyl chains with temperature that determine the intermolecular interactions and the network spacing [2-3].

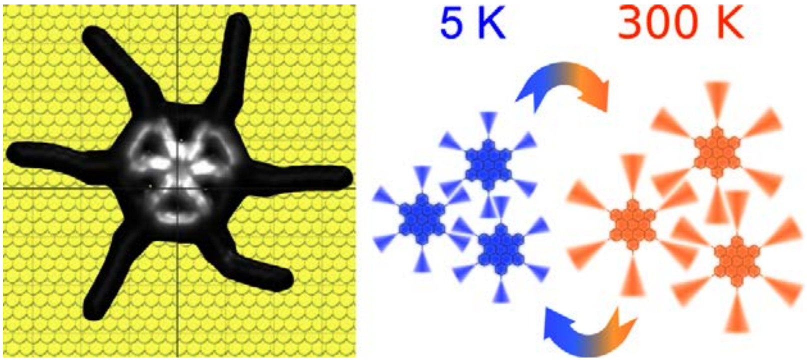

Figure 1. Chemical structure of spoked wheel (SW) molecule equipped with dodecyl chains spray-deposited on Au(111) [1-2].

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# Atomic resolution molecular imaging based on soft-landing electrospray ion beam deposition.

Stephan Rauschenbach

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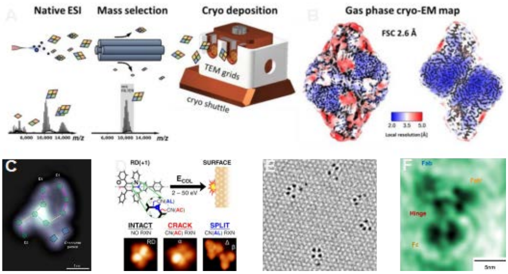
Electrospray ion beam deposition (ESIBD), the deposition of intact molecular ions created by electrospray ionisation onto solid surfaces in vacuum, has been introduced in our lab as a tool for the handling of large and complex, usually non-volatile molecules.[1] Initially, the high-resolution single-molecule imaging by scanning probe microscopy (SPM) has been the major application. Here ESIBD proved successful in the investigation of structure, conformation, and properties of proteins, peptides, saccharides, and synthetic molecules.[2,3]



**Molecular imaging based on ESIBD. (A)** Scheme of native ESIBD deposition onto cryoEM grids.[1] **(B)** 3D density of b-gal prepared by native ESIBD.[5] **(C)** STM image of a branched 11-mer glycan.[2] **(D)** Hyperthermal chemistry: Intact Reichardt's Dye molecule and products of the hyperthermal collision in STM images. **(E)** Transmission electron microscopy of atomic clusters on freestanding graphene. **(F)** Low energy electron holography image of an antibody.

ESIBD's high level of control over molecular ion beam and environment in opens new avenues in molecular imaging. Native ESI enables the chemically selective enrichment of folded proteins and proteins complexes for structural investigation by electron microscopy imaging (cryoEM)[4,5], and low energy electron holography (LEEH).

Optimized conditions for native deposition promote imaging of individual proteins at a resolution sufficient for the construction of atomic models from cryoEM data.[5] The structure obtained from cryoEM after embedding the landed proteins in ice grown from the gas phase shows a fold and subunit arrangement which is remarkably similar to the solution structure. Small conformational changes cause differences mostly at the protein surface and interfaces. We find the closing of cavities and crevices' due to self-interaction in absence of water, a change reversed in MD simulations to find the native structure again.

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# Momentum microscopy & 2D materials: Excitons in space and time

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Transition metal dichalcogenides (TMDs) are an exciting model system to study ultrafast energy dissipation pathways, and to create and tailor emergent quantum phases. The versatility of TMDs results from the confinement of optical excitations in two-dimensions and the concomitant strong Coulomb interaction that leads to excitonic quasiparticles with binding energies in the range of several 100 meV. In TMD stacks consisting of at least two layers, the interlayer interaction can be precisely controlled by manipulating the twist angle: The misalignment of the crystallographic directions leads to a momentum mismatch between the high symmetry points of the hexagonal Brillouin zones. This strongly impacts the interlayer wavefunction hybridization, and, moreover, adds an additional moiré potential. Crucially, in this emergent energy landscape, dark intra- and interlayer excitons dominate the energy dissipation pathways. While these dark excitonic features are hard to access in all-optical experiments, time-resolved momentum microscopy [1] can provide unprecedented insight on these quasiparticles [2-5].

In my talk, I will present our recent results on the ultrafast formation dynamics of interlayer excitons in twisted $WSe_2/MoS_2$ heterostructures. First, I will report on the identification of a hallmark signature of the moiré superlattice that is imprinted onto the momentum-resolved interlayer exciton photoemission signal. With this data, we reconstruct the electronic part of the exciton wavefunction, and relate its extension to the moiré wavelength of the heterostructure. Second, I will show that interlayer excitons are effectively formed via exciton-phonon scattering, and subsequent interlayer tunneling at the interlayer hybridized $\Sigma$ valleys on the sub-50 fs timescale. Finally, I will discuss our recent efforts to monitor the interlayer exciton formation dynamics with spatiotemporal resolution using femtosecond photoelectron dark-field microscopy.

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# Multiscale characterization of functionalized 2D materials: from quantum confinement to embedding of foreign atoms

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The rational functionalization of the physical and chemical properties of two-dimensional (2D) materials is key to their suitability for technological applications. This contribution will focus on two prominent strategies to tailor such properties, i.e lateral confinement and embedding of foreign atoms in single-atom-thick materials. Concerning the first case, the most known example of one-dimensional (1D) lateral confinement is the graphene nanoribbon (GNR), where the nanometer width leads to the opening of an electron bandgap and the formation of spin-polarize edge states. By means of experimental surface-science techniques that span from atomic resolution (Scanning Tunneling Microscopy and Spectroscopy) to micron-scale regimes (Spectroscopic PhotoEmission and Low-Energy Electron Microscopy), and of theoretical calculations, we will demonstrate that such confinement can be achieved without creation of physical edges, i.e. by the creation of 1D structures, incorporated in a continuous, 2D single graphene sheet, that interact differently with the chosen substrate [1]. The so-called graphene “pseudo-ribbons” (GPR) possess the same properties of GNRs and constitutes a topical example for the correct rationalization of lateral confinement in 2D materials. For the second case, i.e. the embedding of foreign atoms, two examples will be discussed: (i) the role of Au atoms in the stabilization of 2D Blue Phosphorus patches epitaxially grown on Au(111) [2], and (ii) the implantation and the characterization of N atoms in single-layer graphene grown via Chemical Vapor deposition on Ir(111) and Ni(111) [3]. Both systems provide crucial information that will be used to prompt a general discussion on the driving forces behind the incorporation of foreign atoms in 2D materials and on their exploitation in the design of 2D materials with technologically valuable properties.

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# Directional motion on surfaces investigated at the single-molecule scale

**G. J. Simpson[1], Mats Persson[2], and L. Grill[1]**

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*[2] University of Liverpool, United Kingdom*

Molecular motion on surfaces plays an important role in many processes such as growth of 2D materials, heterogeneous catalytic reactions, and on-surface polymerisation. According to the principle of microscopic reversibility [1], in a thermally equilibrated system, such motion is random in nature. However, understanding how to control and direct motion of individual molecules is of importance and could lead to the production of novel materials or more efficient catalytic processes.

I will first show how local gradients in the tunnel junction of a scanning tunnelling microscope can result in unidirectional motion. For instance, the inhomogeneous electric field can be used to control the motion of a single molecule via an internal dipole moment. The rotation is found to occur around a fixed pivot point, caused by the interaction of an oxygen atom in the molecule with a silver atom of the underlying surface [2]. The disruption of this anchoring point results in a mixture of rotations and translations, which can be controlled by the choice of manipulation parameters [3].

Of even greater interest are molecular motors which display intrinsic directionality, that is, molecules which convert external energy into a predefined direction of motion. An example of such a system is the well-known Feringa motor. However, such motors often show a reduction or loss of functionality when taken from their native solution phase and deposited onto a metallic surface. In this talk a new concept in molecular motors will be demonstrated, which uses a small and simple chemical structure to achieve perfect unidirectionality when deposited onto a Cu(110) surface [4]. The motion is triggered by switching between two potential energy landscapes, thus avoiding microscopic reversibility, and leads to 100% unidirectionality in the molecule. Furthermore, this unidirectional motion can be harnessed to perform work by transporting small cargo molecules across the surface.

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# Metal-organic and covalently bonded nanostructures on metals and graphene

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With the help of the surface science tool kit fundamental unprecedented information about both the structural and electronic properties of metal-organic coordination networks (MOCNs) as well as covalently coupled organic nanostructures can be obtained. For the latter case of on-surface synthesis, even insight into the reaction processes can be achieved.

In the first part of my contribution, I will focus on the reactivity of the prochiral molecular precursor 6,12-dibromochrysene (DBCh) on different coinage metal substrates. On Au(111), the formation of achiral narrow chevron-like graphene nanoribbons (GNRs) takes place [1]. With scanning tunnelling spectroscopy, we could show that their electronic properties are length- and symmetry-dependent. On the structurally similar Ag(111) surface, four different organometallic phases were found whose formation delicately depends on the substrate temperature during deposition [2]. The thermodynamically preferred phase, 1D heterochiral organometallic polymers, could not be converted into GNRs. We observed chiral selectivity, when keeping the same substrate material but going to a different orientation: on Ag(110) either heterochiral or homochiral organometallic chains form in dependence of the substrate temperature during deposition [3]. On the catalytically more active Cu(111) substrate, DBCh readily debrominates at room temperature, leading to the formation of chiral organometallic polymers which cannot be transformed into GNRs.

In the second part, the structural and electronic properties investigated with scanning tunneling microscopy/spectroscopy and photoelectron spectroscopy will be discussed for cyano-substituted Co-porphyrins (CoTCNPP). The “bare” self-assembled structure on Au(111) [4] is compared to the one on graphene as well as with the formation of MOCNs with Co atoms on both Au(111) and graphene.

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# Visualizing field-tunable flat bands and many-body effects in twisted heterostructures with nanoARPES

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Stacking atomically-thin materials with an interlayer twist angle is a promising method to achieve on-demand quantum materials with emergent properties, including superconductivity, Mott insulators, strange metal and magnetic phases [1-4]. Variation of twist angle, electrostatic doping and material composition provide tuning knobs to control and interrogate the underpinning interactions between electronic states. Here, I will present a new experiment, based on micro- and nano-resolved photoemission spectroscopy (micro- and nanoARPES), that permits direct visualization of the electronic states in twisted two-dimensional materials integrated in device architectures. Specifically, I will discuss flat band dispersions and many-body interactions determined from energy- and momentum-resolved spectral function measurements during field-effect tuning of heterostructures composed of twisted graphene and semiconducting transition metal dichalcogenide layers [5,6].

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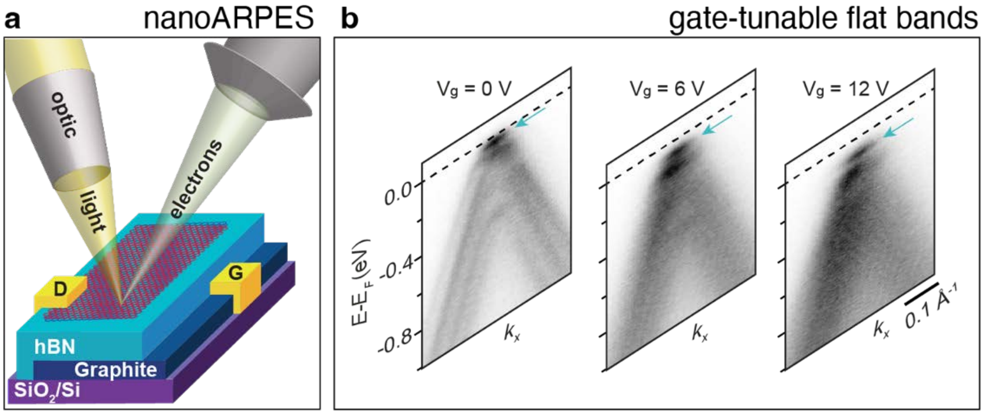

*Figure: (**a**) Schematic of nanoARPES experiment on device composed of twisted 2D materials. (**b**) Visualization of gate-tunable flat bands.*

# Ligation and molecular activation at 2D biomimetic functional materials. A surface science perspective

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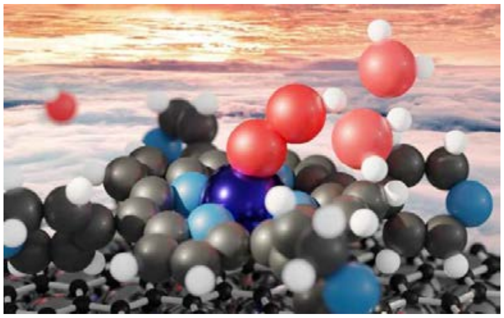

Complex mechanisms underlying the functionalities provided by tetrapyrrolic macrocycles in biochemistry fascinatingly include light harvesting, molecular transport, and catalytic conversion. The main function is often accomplished by single atomic species, caged in the macrocycle embedded in the reaction pocket, with fine-tuning capabilities (band gap, chemical selectivity…) offered by the geometric and electronic structure of the tetrapyrrole, including its residues, and by the proximal and distal structures of the protein surroundings. The artificial replication of both structure and functionality of natural reaction centers in 2D functional materials represents a scientific and technological challenge. Nano-architected 2D metalorganic frameworks can self-assemble under controlled conditions at supporting surfaces. In the specific case, porphyrin- and phthalocyanine-based systems have been widely investigated in ultra-high vacuum conditions by means of surface science approaches, obtaining deep insight into the geometry, electronic structure, magnetic properties, and light absorption with the strong experimental constraint of vacuum. For the interaction of tetrapyrroles with ligands, this limit represents a relevant gap with respect to ambient gaseous or liquid environments and potential applications. Thus, a step forward in this direction is necessary, while maintaining the atomic level detail insight. From the surface science point of view, the characterization *in situ* and *operando* of heme-like, simplified model systems in 2D involves challenges that have been tackled only very recently. I will review findings in this direction reported so far [1,2], with focus on relevant reactions like carbonylation and activation of $CO_2$ [3], $O_2$ activation and reduction (ORR) [4], and the activation of $NO_x$ [5]. We will finally discuss possible perspectives.

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# Soft-Landing meets Mass-Spectrometry - gentle UHV deposition for large, reactive or fragile molecules to create functional nano-architectures

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Cutting-edge research in the field of nanoelectronics, solar technology, catalysis and nano-scale bio-applications requires an unbiased understanding of the structure-related properties of their building blocks. Technically, many restrictions do exist: Thermal evaporation in vacuum (MBE, OMBE) is limited to volatile substances. Solution-based techniques such as drop casting, spin coating or inkjet printing operating in wet environments often lack purity and quality. However, soft-landed building blocks sorted by mass, charge or structure recognition methods play a fundamental and increasing role in such studies. The pool of possible molecules and ionization techniques is exhaustive: The ions are generated from various substances spanning the whole chemical spectrum including single metal atoms or clusters up to larger nanoparticles on one hand, and from small organic molecules up to several kilo- and megadalton proteins, DNA or even entire virus particles on the other hand. Numerous methods such as electrospray, MALDI, laser ablation, magnetron sputtering, plasma techniques and more are established. These diverse sources exhibit a wide range of ionization levels - from singly charged up to several thousand-fold charged. Besides the differences in ion composition and mass to charge ratio (m/z), most ion sources operate at elevated pressures and typically require collimation of the generated ions to a narrow beam and its transfer to higher vacuum for m/z filtering.

In-line with this, we present the development and performance of an ion beam deposition device currently supplied by an ESI-source [1]. Successfully processed examples originating from various chemical groups are presented, comprising GNR, foldamer, porphine derivatives and nucleic acids [2,3]. The main body contains RF-steered ion guides with very high transmission (>80% efficiency). Stacked ring and high order multipoles allow for lowest residual gas loads. Adjustable geometry and diameters down to < 2 mm ensure compatibility with other systems. A digital square-wave quadrupole mass filter provides adjustable amplitude and frequency resulting in a virtually unlimited m/z-range and resolving power, e.g., of >650 m/Δm FHWM at 20 % transmission. The footprint of an entire UHV deposition system is almost benchtop in size, about 50 x 100 cm. Due to its modular nature, all components may easily be integrated/connected to other systems/components.

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# Tuning molecular magnetism and vibrational excitations by supramolecular manipulation

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Molecular magnetism is studied using low temperature scanning tunneling spectroscopy by resolving spectroscopic fingerprints close to the Fermi energy like Kondo resonances, inelastic spin excitations and Yu-Shiba-Rusinov (YSR) states. We find a variety of closed-shell molecules that can become paramagnetic in suitable environments or by molecular switching [1,2]. Furthermore, an unexpectedly large orbital moment related to molecular ring currents is observed. Using YSR states we sensitively detect a large number of molecular vibrations via inelastic tunneling. Magnetic and vibrational excitations are spatially mapped and energy shifts caused by intermolecular interactions are resolved on a 100 µeV scale [3]. Taken together our results highlight the importance of electrostatic stray fields due to polar bonds in molecules.

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# Imaging of conjugated polymers unveiling polymerization defects

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Conjugated polymers (CPs) demonstrate tunable electronic and optoelectronic properties, outstanding biocompatibility and mechanical flexibility, and have been implemented in a wide range of modern technologies [1]. Achieving precise control of the microstructure in CPs is essential for understanding their behavior in high-performance organic electronic devices. However, traditional analytical techniques used in polymer science (XRD, NMR, mass spectrometry, chromatography…) often struggle to precisely characterize modern CPs.

We address this fundamental issue by combining electrospray deposition (ESD), allowing the landing of thermolabile macromolecules on surfaces in ideally controlled conditions [2], with low temperature scanning tunneling microscopy (LT-STM). Aldol condensation is an important reaction frequently used in organic synthesis, and the resulting CPs show excellent electronic properties to be employed in advanced (bio)electronic devices [3]. In this work, a few CPs synthesized by aldol condensation were characterized. Our ESD-STM technique allows to acquire sub-monomer resolved images of rigid rod CPs, revealing their composition and structure at a level that is so far impossible with any other present analytical techniques [4-6].

Unexpected polymerization defects were demonstrated, appearing both as deviations from the ideal polymer sequence and as kinks in the backbone structure that had not been considered so far in the literature. Detailed reaction pathways leading to the formation of the observed defects are proposed. The results bear a high potential impact for their implications in understanding the reaction mechanisms of aldol condensation reactions at the molecular level.

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# Abstracts of Posters

(in alphabetical order)

# Unveiling Periodicities: Nonreciprocal CDW Proximity Effects in Monolayer $NbSe_2$/$TiSe_2$ Heterojunctions

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Lateral heterostructures between two-dimensional (2D) transition metal dichalcogenides are highly interesting since they have potential applications for constructing monolayer electronic devices. Such in-plane heterostructures are also ideal systems for exploring the interfacial effects on quantum phases, such as charge-density wave (CDW) order in the true 2D limit. Here, we report on a lateral CDW heterojunction made of monolayer $NbSe_2$ and $TiSe_2$ with atomically sharp interface. Scanning tunneling microscopy reveals an unexpectedly nonreciprocal CDW proximity effect at the $NbSe_2$ vicinity of the heterojunctions: the $(2 \times 2)$ CDW order of $TiSe_2$ is found to propagate into the $NbSe_2$ side of the heterostructure, while the $(3 \times 3)$ CDW order of $NbSe_2$ resides in the $NbSe_2$ side. Such a nonreciprocal CDW proximity effect indicates that the quantum phase of electrons in $NbSe_2$ can be easily tuned by the adjacent $TiSe_2$. Our study highlights the significance of quantum interfacial effect in lateral heterojunctions, which may help for constructing tunable 2D in-plane quantum devices based on proximity effects or in-plane interfaces.

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# Assisted on-surface synthesis of porous graphene nanoribbons on vicinal surfaces

**P. Angulo-Portugal[1], M. Sarker[2], I. Piquero-Zulaica[3], Z. M. Abd El-Fattah[4], F. Schiller[1,5], D. G. de Oteyza[5,6], A. Sinitskii[2] and M. Corso[1,5]**

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Carbon-based nanoporous systems hold great potential as sensors since pores may act as anchoring sites for small analytes. Recently, periodic defects (pores) were introduced in the graphene lattice, producing 1 eV semiconductor nanoporous graphene [1]. Theoretical studies predict the tunability of the electronic response of porous armchair graphene nanoribbons (PGNRs) by controlling the size and shape of pores, making them suitable materials for sensing devices. In this work, we explore the growth of 12-atom-wide PGNRs on vicinal Au(111) surfaces using scanning tunneling microscopy (STM) and explore their electronic structure via angle resolved photoemission spectroscopy (ARPES). After the on-surface synthesis of 12-PGNRs we observe a preferential growth aligned along the [11-2] direction, parallel to the steps of kinked Au(654) surfaces. On vicinal Au(788), step alignment is only achieved if the ribbons' growth is guided by poly(para-phenylene) chains. The band structure of 12-PGNRs grown on Au(788) and kAu(654) was probed by ARPES (E vs $k_y$) showing a well-defined dispersive band parallel to the steps [ΓK direction of the Au(111) terraces] at -1 eV centered at $k_y$=1.5 $A^{-1}$. This study opens up the possibility of utilizing a new and promising family of porous GNRs that could be further expanded following a similar approach with modified molecular precursors to obtain wider porous GNRs or to explore doping effects.

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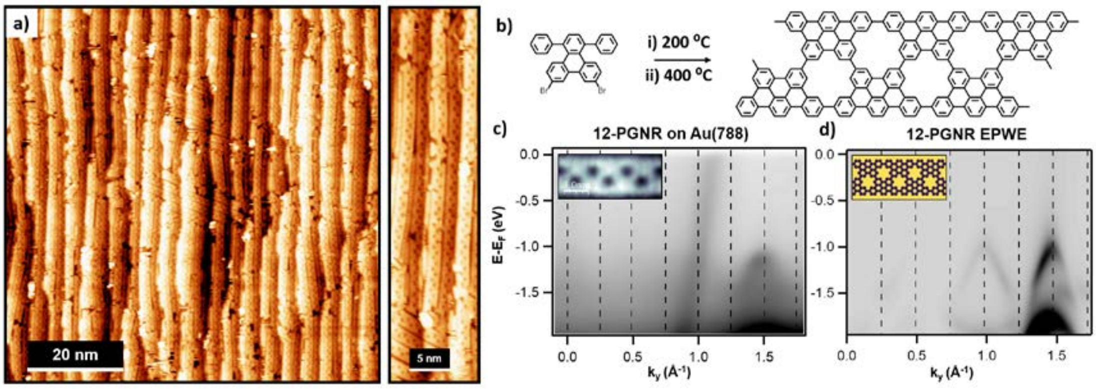

**Figure**. **a**) RT-STM of 12-PGNRs grown on Au(788). **b**) Scheme of 12-PGNR synthesis. **c**) ARPES electronic band structure. **d**) Electron-plane-wave-expansion spectral weight simulation.

# Controlling Yu-Shiba-Rusinov States in Supramolecular arrays using Molecular Switches

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Ordered arrays of functional molecules may be an ultimate limit of miniaturization for future electronic devices. Tin phthalocyanine (SnPc) is a prototypical representative of functional molecules. It is diamagnetic in gas phase, non-planer, and geometrically bistable on metal surfaces where transitions can be induced by electron or hole injection[1]. Here we probed SnPc on superconducting Pb(100) using low-temperature scanning tunneling spectroscopy. Yu-Shiba-Rusinov (YSR) states are observed - upon assembly of the individual adsorbates into supramolecular arrays, which indicates the presence of a molecular spin[2]. In addition, the effect of geometrical switching on the spatial distribution of YSR states in the supramolecular architecture is demonstrated.

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# Growth and characterization of sharp, atomically flat graphene/oxide heterojunctions

**Michele Capra[1], Andrea Picone[2], Alberto Brambilla[2], Sara Fiori[3], Deepak Dagur[3], Giovanni Vinai[3], Piero Torelli[3], Giancarlo Panaccione[3], Paolo Moras[4], Marco Finazzi[2], Franco Ciccacci[2], Lamberto Duò[2].**

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Tailored by the discovery of the first bidimensional material, Graphene, characterized by novel, unmatched electronic and mechanical properties, huge effort has been spent in order to investigate the existence of other low dimensional materials. During the last decades, scientific communities has mainly focused on the study of layered and elemental bidimensional materials (like transition metal dichalcogenide, Stanene, Silicene etc.), paying little attention on the synthesis and properties of low dimensional oxides. The ability to combine electronic and magnetic properties offered by transition metal oxides, like antiferromagnetism and magnetoelectricity, with high scalability and novel phenomena offered by 2D systems due to quantum confinement, may set the way for the development of new integrated systems. In this presentation we describe a procedure for exploiting Graphene as buffer layer for both intercalation of transition metal and rare earth atoms, and subsequent oxidation for the synthesis of high quality, atomically flat, oxides[1-3]. Synthesis of sharp graphene-oxides heterojunctions is a challenging task (due to the extremely low graphene surface free energy) which may open the possibility of achieving the electrical control of graphene, exploiting the oxide layer as an insulating gate.

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# On-Surface Synthesis of Peripherally Oxygen-Annulated Porphyrins

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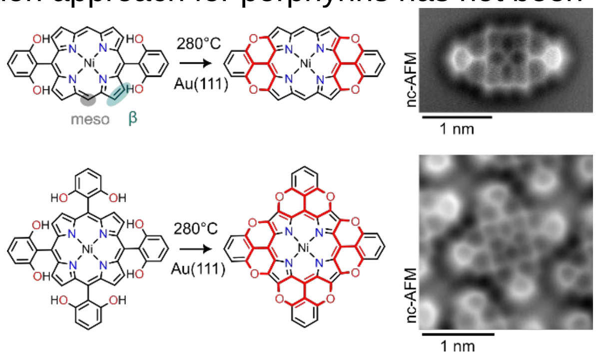
Recently the on-surface synthesis of fused porphyrins displaying various edges and topologies has generated considerable interest [1,2]. Fused porphyrins are commonly prepared through C-C bond formation reactions exploiting dehydrogenative (from C-H) and dehalogenative (from C-Br and C-I) pathways. Such procedures offer precise control over the (electronic) structure of the porphyrin products and can even lead to π-electron magnetism [3,4]. From a chemistry point of view, the toolbox is currently limited to C-C coupling, and on-surface C-heteroatom bonding as planarization approach for porphyrins has not been demonstrated so far.



Embedding heteroatoms in the extended π-system of porphyrins tailors their electronic, optical and assembly properties, offering a promising path to develop functional materials. In this context we explored the on-surface oxygen annulation of Ni(II)-tetra- and octahydroxyporphyrins on Au(111). Upon thermal activation the ortho-positions of the meso-aryl substituents (dihydroxyphenyls) are connected by an O-bridge to the β-pyrrolic positions of the porphyrin macrocycle, creating pyran rings. Employing STM, nc-AFM and high-resolution XPS, we provide a comprehensive characterization of the on-surface reaction. Beyond that, we elucidate how the oxygen tailors the electronic structure and drives the assembly of the achiral molecules into chiral lattices.

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# Tuning quantum electronic transport and anisotropy in nanoporous graphene

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Bottom-up on-surface synthesis techniques have allowed the realization of atomically precise nanometer wide graphene nanoribbons (GNRs). More recently, the lateral covalent coupling of width-modulated GNRs led to the fabrication of atomically precise nanoporous graphene (NPG) [1]. Besides being a semiconductor, this novel 2D material exhibits a highly anisotropic electronic structure, which makes NPG appealing to control currents at the nanoscale. In particular, NPG can be thought as a lateral array of weakly coupled semiconducting nanochannels, where electrons propagate according to the so-called Talbot interference effect [2]. Furthermore, such interference pattern could be controlled by modifying the atomic structure and chemical composition of the phenylene bridges connecting adjacent GNRs [3].

In this work, we present the on-surface synthesis of a new NPG structure, in which atomic scale modifications of the phenylene bridges lead to three different inter-ribbon coupling configurations: “para-para”, “para-meta” and “meta-meta”. Our Density Functional Theory (DFT) calculations, supported by Scanning Tunneling Microscopy (STM) characterization, predict different anisotropic behaviours for each of the three possible chemical coupling configurations. Additionally, the twist of phenylene groups in “para-para” bridges acts as a fine-tunable knob to control the electronic anisotropy of NPG. These results are complemented by quantum electronic transport simulations, which show dramatic changes in the interference pattern emerging from charge-carrier propagation. Our findings demonstrate that molecular bridge engineering is an efficient approach to optimize electronic anisotropy and control nanoscale currents on NPG [4].

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# Investigation of structural and magnetic properties of ceramics $Sr_3Fe_{2+x}Mo_{1-x}O_{9-3x/2}$ ($x = 0.45, 0.60$, and 1)

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Perovskite oxides $Sr_3Fe_{2+x}Mo_{1-x}O_{9-3x/2}$ ($x = 0.45, 0.60$, and 1) were synthesized in polycrystalline form using solid–state reaction route, in air [1]. The crystal structure of these compositions was resolved and refined using the Rietveld method, and revealed that ($x = 0.45$ and 0.60) adopt a tetragonal space group *I*4/*mcm*; while ($x = 1$) adopts another tetragonal space group *P*4/*mmm*.

The magnetic measurements were carried out using superconducting quantum interference device (SQUID) sensor (MPMS-XL-7AC, Quantum Design). Magnetization as a function of the applied magnetic field was made for temperatures $4.2 \leq T \leq 156$ K, with a maximum applied field up to 5 T.

We investigate in detail the magnetic, magnetocaloric properties and phenomenological model of perovskite type: $Sr_3Fe_{2+x}Mo_{1-x}O_{9-3x/2}$ ($x = 0.45, 0.60$, and 1) [2]. With a Curie temperature from 132 to 144 K, the magnetic transition nature undergoes a secondorder magnetic phase transition from ferromagnetic to paramagnetic states. We have used the thermodynamic Maxwell relation to determine the magnetic entropy change ($-\Delta S_M$) in the studied compositions. Moreover, we report a theoretical investigation of the magnetocaloric effect using a phenomenological model. The model parameters and their variation with temperature and the magnetic field were obtained. The theoretical predictions (adopted model) were found to be consistent with the experimental results.

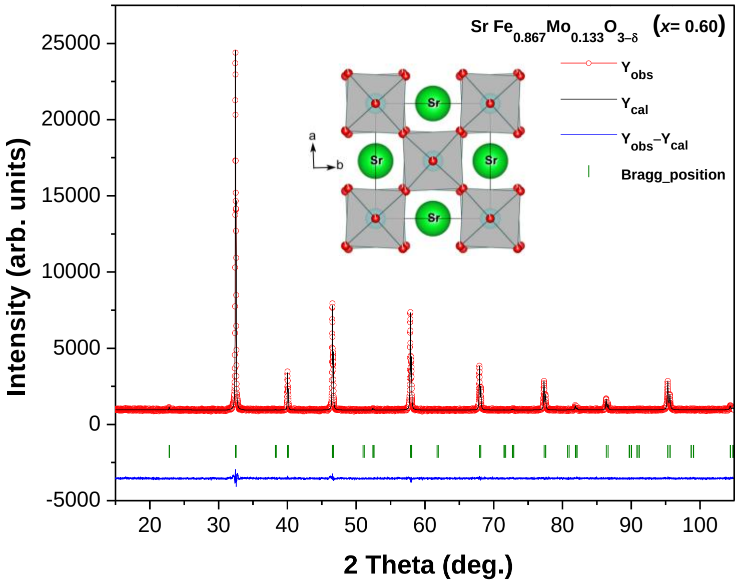

Fig.1: Final Rietveld refinement plot.

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# Voltage-Gated Reversible Switching of Moiré Patterns in Organic Two-Dimensional Molecular Crystals

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Two-dimensional (2D) molecular crystals are a class of ultrathin materials composed by highly ordered molecular arrays with uniform in-plane orientation, resulting from the assembly process of organic molecules on crystalline surfaces.[1] An interesting property of two or more superimposed 2D-crystals is the formation of interferences, generally called Moiré patterns, as a consequence of rotation or translation of at least two spatial frequencies of one layer in respect to the other, leading to the formation of completely new topologies. For inorganic 2D-crystals such as twisted bilayer graphene, Moiré patterns are well studied and give rise to unconventional new electronic structures and properties, including the appearance of superconductivity. However, for organic-inorganic vdW heterostructures Moiré patterns gained only little attention due to the difficulty of experimentally predict these phenomena as well as investigate the properties such as, for example thermodynamic stability and control at the nanoscale.[2],[3] Herein, we describe the formation of extended organic-inorganic Moiré patterns on HOPG at the solid-liquid interface, characterized by HR-Scanning Tunneling Microscopy. Surprisingly, by tuning the orientation of the external electric field of the STM tip, a supramolecular re-organization of the organic 2D-crystal was observed with consequent loss of the previously observed Moiré pattern. Formation and loss of Moiré patterns was found to be reversible and highly reproducible, providing full control over the 2D-molecular crystal at the nanoscale. A detailed mechanistic understanding of the structural reorganization has been obtained by combining STM imaging and molecular dynamics (MD) simulations. This new process opens the way to the first reversible switching of Moiré patterns in organic-inorganic vdW heterostructures and provides a deeper understanding of the thermodynamics and kinetics of incommensurable 2D-crystal lattices.

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# On-surface reactions of triazido-*s*-heptazine

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2,5,8-Triazido-*s*-heptazine is an aromatic molecule containing only carbon and nitrogen atoms. Heptazine core functionalized with reactive azido-groups makes it an interesting candidate as a precursor for on-surface synthesis of graphitic carbon nitride, an important 2D material [1]. The challenge in this approach is that there are several alternative reaction pathways, which are difficult to control, due to the high reactivity of the aromatic azides [2].

Here, we study these molecules by low temperature scanning tunneling microscopy (STM) under ultra-high vacuum conditions, which allows to study changes in single molecules induced by different impacts. Molecular transformations are induced either by voltage pulses from the STM tip or by illumination with UV light. In each case, we observe two types of processes. Short illumination or short voltage pulse induce dissociation of the azido-group into a nitrogen and a nitrene molecule. On the other hand, longer illumination times lead to drastic increase of the apparent height, which will be discussed in view of other options, for instance the formation of another product or different adsorption configurations.

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# Investigating the Role of ITO Substrate and Sample Condition in Electronic and Optical Properties of $WSe_2$ Monolayers

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Monolayers of transition metal dichalcogenides (TMDs), belonging to 2D materials, have a great potential for applications in optoelectronic devices due to reduced thickness and promising properties. Monolayers of $WSe_2$ are particularly interesting because they feature a direct electronic band gap emitting a very intense light in the visible range. Depending on the substrate[1,2], the luminescence and the electronic properties of the monolayer can be altered, thus understanding this interaction is essential for future applications.

In this study, we investigated the role of indium tin oxide (ITO) substrate on the optical and electronic properties of the $WSe_2$ monolayer in ambient conditions and vacuum. During the measurements, it was considered the influence of adsorbates by performing an annealing step. The adsorbates are localized at the interface between the exfoliated TMD layer and the substrate and their presence has been characterized before[3]. To confirm the presence of the adsorbate layer the height of the step between the monolayer and the ITO was measured. After annealing the step height decreased, indicating the removal of the adsorbed layer. The density of states of the $WSe_2$ monolayer changed upon annealing, signaling a change in doping. The surface potential probed by Kelvin Probe Microscopy changed in polarity, likely due to a band alignment change or removal of polar molecules. The photoluminescence intensity and doping changed after the annealing and at different conditions.

This study shows that the ITO substrate and adsorbates have significant implications in the band alignment and luminescence. Such effects are expected to play a role also in the studies exploring luminescence induced in a scanning tunneling microscope.

Acknowledgments: Funded by CAPES and FAPESP (Project 2021/06893-3).

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# Measuring and Mapping Elongation of Single Helicene Molecules by NC-AFM

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Non-contact atomic force microscopy (NC-AFM) has become a standard tool for the investigation of individual atoms and molecules on surfaces. However, the measurement of elasticity in single molecules and its submolecular resolution have remained as a largely open question. To address this issue, a spring molecule - nonahelicene ([9]H) - was investigated and compared with its flat counterpart - coronene (cor). The molecules were imaged first by high-resolution scanning tunneling microscopy (STM) and NC-AFM on a Ag(110)-surface at cryogenic temperatures (4.8 K) and ultrahigh vacuum (UHV) conditions. Interactions of metallic tips with [9]H and cor and the associated elongations were studied then by frequency shift- distance measurements. A novel model for the description of the NC-AFM signals considering an elastic response in the molecular spring was utilized subsequently to rationalize the behavior of both molecules. The spring constant of [9]H was thereby successfully determined to be 5.6 N/m. Mapping the response above the [9]H molecule was performed then to resolve the elastic component with submolecular resolution. The results demonstrate NC-AFM as a powerful tool for the detection of deformation on the atomic scale.

# Exploring the structural and chemical composition of antimony monolayer on Ag(110)

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The unique characteristics of silicon nanowires have generated significant interest in developing comparable structures using alternative materials. Especially heavier elements such as Sn, Sb, or Bi are interesting materials due to their spin-orbit coupling, making them promising candidates for topological insulators. This study focuses on antimony, which has already been fabricated in a nanowire arrangement on Ag(111) [1].

However, the preparation on a (111) surface raises the question of whether the row-like arrangement of the Ag(110) surface is more suitable for the preparation of nanowires. The electronic properties and structural arrangement of the adsorbat are highly dependent on the surface and interface structure of the system. Consequently in our study we focus on investigating the surface and interface of the Sb/Ag(110) system.

This study investigates the impact of layer-thickness and annealing temperature on the structural and chemical composition of the monolayer Sb-phases. Therefore we use surface sensitive methods, namely low-energy electron diffraction (LEED), X-ray photoelectron spectroscopy (XPS), and scanning tunneling microscopy (STM).

Our results show a dependence on both, temperature and layer-thickness, with different structural and chemical arrangements. The chemical composition of antimony monolayers on Ag(110) presented in this study has not been previously reported to our best knowledge. For different layer thicknesses, three chemically distinct phases were identified through XPS measurements, even though two of them appeared structurally identical in LEED with a c(2x2) reconstruction. Additionally, it was discovered that the XPS component to the c(2x2) structure is only weakly bound to the Ag substrate. While the first c(2x2) reconstruction was obtained for a coverage of 1/4ML, the second c(2x2) phase was identified as a transition phase to the third observed phase. The third phase was obtained at higher coverage with a distinct and quite complex structural arrangement in LEED. The results of the higher coverage phase are consistent with the discovery of Sb-nanostrips by Wang et al..

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# Probing molecular conformation via photoemission orbital tomography

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Porphyrins offer a wide range of tunability and play a key role in vital biological functions such as oxygen transport and photosynthesis. On proper surface templates, they can be confined in two-dimensional arrays, where the chemical state and adsorption properties of the molecules are well-defined and homogeneous. However, the resulting molecule-substrate interaction can induce electronic and conformational changes, affecting the molecular layer's chemical reactivity, crucial for use in organic-based devices.[1] Here, by means of photoemission orbital tomography - a technique that combines momentum-resolved photoemission spectroscopy and density functional theory - we investigate the electronic and geometrical structure of two metalated tetraphenyl porphyrins (MTPPs), namely ZnTPP and NiTPP, adsorbed on the oxygen-passivated Fe(100)-$p(1 \times 1)$O surface.[2] The absence of charge transfer suggests a weak electronic interaction between the molecules and the surface, yet the molecular layers exhibit varying levels of macrocycle distortion. In the case of ZnTPP, our data correspond to those of moderately distorted molecules whereas NiTPP exhibits a severe saddle-shape deformation. From additional experiments on NiTPP multilayer films, we conclude that this distortion is a consequence of the interaction with the substrate, as the NiTPP macrocycle of the second layer turns out to be flat. We further find that distortions in the MTPP macrocycle are accompanied by an increasing energy gap between the highest occupied molecular orbitals (HOMO and HOMO-1). Our results demonstrate that photoemission orbital tomography can simultaneously probe the energy level alignment, the azimuthal orientation, and the adsorption geometry of complex aromatic molecules, not only for monolayers, but also in the multilayer regime.

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# Coverage-modulated halogen bond geometry transformation in supramolecular assemblies

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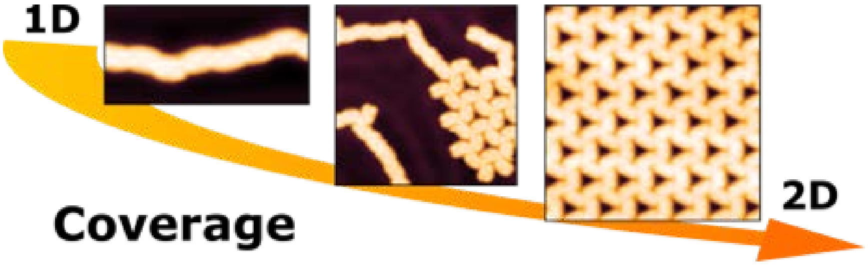
Halogen bonding (HB) has emerged as a promising route for designing supramolecular assemblies due to its directional nature and versatility in modifying interactions through the choice of halogen and molecular entities.[1] Despite this, methods for tuning these interactions on surfaces, particularly in terms of directionality, are limited. In this study, we present a strategy for tuning the directionality of self-assemblies depending on the molecular coverage. Our results indicate that under lower molecular coverage conditions, robust one-dimensional (1D) structures promote the self-assembly of halogen bonding is observed, leading to an extended hexagonal pattern of molecular assembly. The atomistic details of the structures are experimentally studied using high-resolution atomic force microscopy and supported by first-principle calculations. We employed density functional theory to evaluate the interplay between electrostatics and dispersion forces driving both type-I and synthon assemblies. The results reveal a halogen-bond geometry transformation induced by a subtle balance of molecule-molecule interaction. Finally, we investigate the capability of the halogen-bonded supramolecular assembly to periodically confine electronic quantum states and single atoms. Our findings demonstrate the versatility of sigma-bonding in regulating molecular assembly and provide new insights for tailoring functional molecular structures on an inert metal substrate.[2]



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# Adsorption Behavior of N Heterocyclic Carbene with Thiophene on Au(111)

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This research delves into the adsorption and rotation characteristics of 1,3-diisopropyl-6-(thiophen-2-yl)-1H-benzo[d]imidazole-3-ium-2-carboxylate (NHC$^{i}$Pr-T) on an Au(111) surface, employing Low Temperature Scanning Tunneling Microscopy (LT-STM) in Ultra High Vacuum (UHV). The molecule under investigation displays two chiralities and adsorbs flat on the surface with a gold adatom at the carbene carbon. The molecule also demonstrates chirality-independent rotation around Sulphur upon voltage pulses with the STM tip.

# Unravelling Glycan Structures: ESIBD+STM Exploration of Stapled Conformations

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"Function follows form" holds a particular significance in the realm of biomolecules, where structural modifications can profoundly influence functionality. Recently, introduction of linkages or 'staples' at specific sites within a linear oligosaccharide (*a.k.a.* glycan) has been demonstrated to alter the biochemical properties of the glycan [1]. Despite these advancements, the structural effect of these staples on glycan conformation has yet to be probed directly, leaving the bioactive conformations unknown.

Using Electrospray Ion Beam Deposition (ESIBD), we successfully transferred these stapled glycans onto a surface in vacuum, which are subsequently imaged individually by Scanning Tunnelling Microscopy (STM). By systematically varying factors such as stapling length and sites, we can visualize the possible conformational states of these stapled glycans. This integrated ESIBD+STM approach provides a complementary tool for studying biomolecular conformational states at the single-molecule level, overcoming limitations of conventional techniques.

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# Single molecule manipulation for Scanning Quantum Dot Microscopy tip functionalization

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Scanning Quantum Dot Microscopy (SQDM) [1], a variant of scanning probe microscopy (SPM), enables the quantitative mapping of the electrostatic potential at the atomic scale [2,3]. Essential for SQDM is the tip functionalization with a nanoparticle that enables quantum confinement and, thus, acts as a quantum dot (QD). This functionalization of the SPM tip has so far been achieved by attaching a single isolated 3,4,9,10-perylene-tetracarboxylic-dianhydride (PTCDA) molecule to the tip in a well-defined manner [4].

We developed a two-step procedure for this SPM tip functionalization based on controlled lateral and vertical manipulation of a single PTCDA molecule on Ag(111) at 5K under UHV conditions with a combined scanning tunnelling (STM) and atomic force (AFM) microscopy system.

The first step focusses on the lateral isolation of a single PTCDA molecule. After establishing a bond between the metallic STM tip and one of the molecule carboxylic oxygen atoms, the molecule can be dragged away from the edge of a PTCDA island. Ensuingly, the bond is cleaved again to release the molecule. From our observations, we were able to separate this cleaving process into two distinct cases of breaking the tip-molecule bond either actively or passively.

The second step concerns the vertical manipulation of the previously isolated PTCDA molecule. For the functionalized tip to exhibit QD properties, the molecule must be lifted in a controlled manner. This is achieved by again forming a bond between the tip and the carboxylic oxygen atom and then lifting the tip along a specific trajectory above the (contacted) molecule. We manually performed this critical step by utilizing a 3D real space positioning controller.

With this two-step procedure, we are able to prepare SPM tips functionalized with single PTCDA molecules ready for conducting SQDM measurements.

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# Bottom-up Fabrication and Scanning Probe Microscopy Characterization of Graphene Nanoribbons

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Graphene nanoribbons (GNRs) are quasi-1D graphene strips that exhibit novel properties deriving from electron confinement and related band gap tunability. Tuning GNRs' electronic and magnetic properties at the single-atom level makes them ideal for diverse device applications, including field-effect transistors (FETs) (*1*) and spintronics. The length and ambient stability of GNRs also play a crucial role in their device integration (*2*).

In this poster, I present how we grow atomically precise GNRs with distinct edge configurations, through surface-assisted polymerization and cyclodehydrogenation of specifically designed organic precursors. Scanning probe microscopy and Raman spectroscopy are extensively used to characterize the quality of GNRs. To bring GNRs from ultra-high vacuum (UHV) to device integration, they are transferred from the gold substrate to device substrates using different transfer methods, including wet-processes such as polymer-free and/or an electrochemical delamination method, as well as semi-dry/dry-transfer methods.

In collaboration with our device partners, we made important progress by integrating different armchair GNRs (AGNRs) into FETs with different gate and contact configurations. I will present our latest transport measurements on 9-, 5- and 17-AGNRs in different device configurations using graphene and metal electrodes. We show that long 5-AGNRs (>20 nm) FETs with Pd as contacts behave as a semiconductor, with $I_{on}/I_{off}$ ratios of $\sim 10^3$. Using 9-AGNRs as channel material, we showcase FETs with high on-current $I_{on}$ > 12 µA at $V_d$ = -1 V and high $I_{on}/I_{off}$ ratios of $\sim 10^5$ along with device yield of 80-100%.

Moving beyond AGNRs intended for traditional FETs, I will share the prospective and our preliminary results of other edge-extended GNRs. With novel functionality, including spin-polarized edge channels and topological quantum states, such GNRs hold tremendous potential in spintronics and quantum computing devices.

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# Distance-Dependence of Orbital Density Imaging Using a CO-Functionalized (p-wave) STM Tip

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In scanning probe methods, knowledge about the tip apex is indispensable to reliably identify the structure and electronic properties of surfaces and adsorbed molecules.[1] In particular, well-defined, CO-terminated tips are widely used to achieve atomic resolution in atomic force microscopy.[2] In scanning tunneling microscopy (STM) the defined geometry and states of a CO tip apex enable high-resolution mapping of ionic resonances, and resulting orbital density images reflect a mix of s- and p-wave symmetries of the CO tip states.[3-5]

In this work, we study the appearance of frontier molecular orbitals of pentacene on bilayer NaCl grown on Cu(111) as a function of the tip-sample distance and bias voltage. STM constant-height imaging reveals a transition from p- to s-wave dominated tunneling upon increasing the tip-sample distance. The contrast change is explained with the symmetry-dependent decay lengths of the tunneling matrix elements. Our findings allow for reliable identification of a molecule's electronic and spin states, which often requires STM imaging of orbital densities and careful assignment to calculated molecular orbitals.[6]

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# Reactivity of single metal atoms in different coordination environments

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Metal centers within metalorganic networks hold promise for applications in single-atom catalysis, gas storage and sensing. Their activity is not only determined by the chemical nature of the metal, but is also significantly influenced by the bonding configuration. It is of fundamental scientific and technological relevance to understand how the reactivity of these sites can be controlled via chemical design.

In this work we present direct measurements of the interaction forces of single metal atoms[1,2] in different metalorganic coordination environments via atomic-scale atomic force microscopy (AFM) experiments. In particular, we examine how the interaction of metal sites with different types of probe atoms (that are directly attached to the AFM tip) changes as a function of their bonding configuration. Our measurements show that while chemically rather inert CO-functionalization yields little discrimination between the metal centers in different environments, Cl-functionalization gives rise to significant differences: low-coordinated metal atoms exhibit notably stronger interactions with the probe atom.

Such atomic-scale studies provide means to characterize active sites within complex metal-organic architectures, thus aiding in a rational design strategy towards materials with tailored catalytic properties.

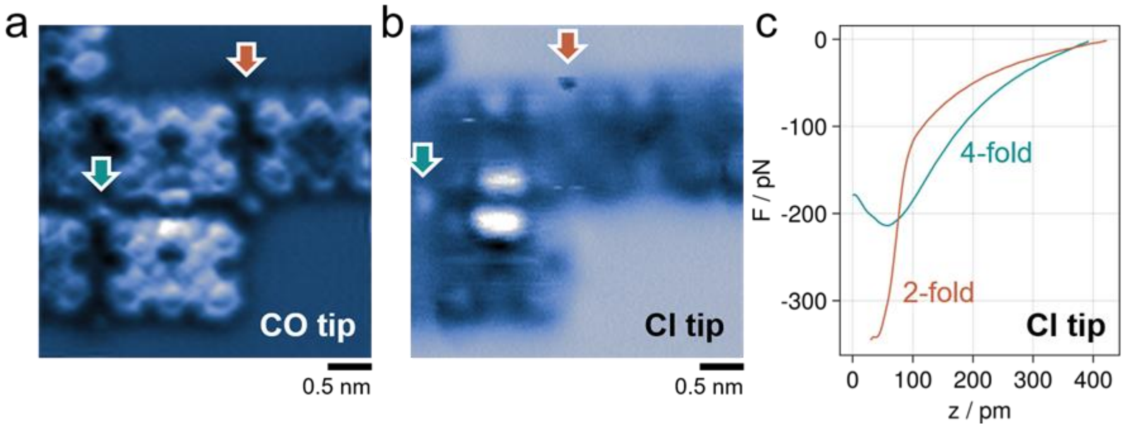

**Figure 1. Interaction of Fe atoms at different sites in metalorganic networks with functionalized AFM tips.** Constant height AFM images acquired with **(a)** CO- and **(b)** Cl-functionalized tips. **(c)** This behavior is reflected in the force-versus-distance curves: the curve taken at the twofold coordinated site (orange color) shows a substantially deeper local force minimum (i.e., stronger attraction) compared to the fourfold coordinated site (green color).

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# Engineered quantum states in assembled van der Waals heterostructures

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The assembly of van der Waals (vdW) materials into heterostructures enables the engineering of exotic quantum states by moiré and proximity effects. The resulting properties are typically well accessible on the heterostructure surfaces, such that scanning tunneling microscopy (STM) has become an important tool for their structural and electronic characterization. While the possibilities to combine individual vdW layers are virtually infinite, the fabrication of samples with atomically clean surfaces, as required for high-resolution STM studies, was typically limited to air-stable or epitaxially grown samples. In my talk, I will summarize our developed vdW assembly methods [1], which allow the stacking of air-sensitive vdW materials with atomically clean surfaces and internal interfaces, and will show results of proximity heterostructures [2,3] and twisted bilayers [4].

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## Acknowledgements

The work was supported by the German Research Foundation's (DFG) Emmy Noether Programme and Priority programme 2244 ('2D Materials – Physics of van der Waals [hetero]structures', project nos. 443416235 and 422707584); the Alexander von Humboldt Foundation; Germany's Excellence Strategy - Cluster of Excellence Matter and Light for Quantum Computing (ML4Q); European Union's Horizon 2020 Research and Innovation Programme under Grant Agreement no 824109 (European Microkelvin Platform); the Helmholtz Nano Facility; APVV-20-0425, VEGA 2/0058/20, Slovak Academy of Sciences project IMPULZ IM-2021-42, COST action CA21144 (SUPERQUMAP) and EU ERDF (European regional development fund) Grant No. VA SR ITMS2014+ 313011W856.

# Unraveling the influence of ferroelectricity on oxide perovskite surfaces and their photocatalytic reactions

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Perovskite oxides have gained much interest in recent years due to their diverse physical and chemical properties. Some of them are known for their excellent performance in photocatalysis and piezocatalysis, among others thanks to their ferroelectricity [1]. It was already shown that the ferroelectricity of a perovskite has an impact on the surface structure and its reactivity and this issue is currently widely researched [2]. Despite this, the origin of such properties remains insufficiently understood and awaits further research.

This work investigates the differences in morphology and ferroelectric polarization at surfaces of incipient ferroelectric $KTaO_3$(001) and ferroelectric $KNbO_3$(001) and $BaTiO_3$(001) crystals after in-situ and ex-situ cleaving. Surfaces of as-cleaved perovskites exhibit (1x1) bulk-termination and adopt (2x1) after exposure to vapor water in ultra-high vacuum (UHV) conditions. Different microscopy methods, like AFM, and STM as well as LEED diffraction were applied to observe changes in the surface reconstruction, whereas the polarization camera imaging and SEM microscopy were used to obtain information on the large-scale ferroelectric domain structure. This poster aims to show the influence of ferroelectricity on the surface after reaction to different amounts of water. Furthermore, open-circuit photocurrent measurements were conducted on powdered perovskite crystals, both paraelectric and ferroelectric, to assess their photocatalytic abilities under ambient conditions.

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# Detailed structural information of conjugated polymers revealed by high resolution scanning tunnelling microscopy

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Conjugated polymers (CPs), within organic semiconductors have attracted significant attention, due to their remarkable conductivity, mechanical flexibility, and cost-effective processability. These attributes position CPs as highly promising candidates for a broad variety of applications, including optoelectronics, thermoelectrics, sensors and bioelectronic devices [1-2].

The innovative combination of electrospray deposition (ESD) [3] with scanning tunnelling microscopy (STM) in an ultrahigh vacuum environment, a recent advancement from the Costantini Group [4], offers an unprecedented opportunity to gain detailed, molecular-scale insights into the structure, conformation, and assembly of surface-adsorbed conjugated polymers. This level of analysis remains unattainable by any other existing analytical technique. The electrospray ionisation process enables the controlled and intact soft-landing of sub-monolayer coverages of CPs onto atomically clean and flat single crystal surfaces, while preserving the CP original sequence and structure. The resulting surfaces are analysed by high-resolution STM, which provides direct evidence about the preferential assembly configurations of CPs, their stacking distances, the polymer mass distributions, the exact backbone sequences and the side chain conformations [5].

Our current study focuses on the benchmark polymer pBTTT [6], which is known for its (semi)crystalline microstructure and impressive charge carrier mobility [7]. Specifically, we endeavour to compare two variations of pBTTT, with mixed alkyl and alkoxy side chains, synthesized through the conventional Stille polymerization method, and the other through an alternative oxidative homopolymerization method anticipated to yield fewer defects. This in-depth structural analysis, surpassing the capabilities of standard analytical techniques within polymer science, proves indispensable in establishing a robust structure-function relationship. It also is essential in determining reliable structure-function relationship and sets the stage for the development of novel, more environmentally friendly and enhanced synthetic polymerization strategies for this crucial category of functional materials.

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# Electrospray Ionization Ion Beam Deposition of Organic Molecules

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When studying large molecules on surfaces, the deposition process can often be a limiting factor. While small molecules can usually be thermally evaporated using a Knudsen cell, the vapor deposition of larger molecules may be hindered by their low vapor pressure, especially if the molecules have labile functional groups. One approach to overcome these preparation-related limitations is electrospray ionization ion beam deposition (ESI-IBD). While this technique is becoming increasingly popular, for example in the preparation of large biomolecules, the precise chemical state of the deposited molecules is often unknown. For this study, we chose meso-tetraphenylporphyrin as a well-known model system to investigate the chemical state of the molecule after deposition via ESI-IBD. X-ray photoelectron spectroscopy (XPS) indicates the presence of an N-protonated species. By utilizing scanning tunneling microscopy (STM), we observed self-assembled islands composed of multiple distinguishable species, in agreement with the existence of N-protonated porphyrin molecules.

# Nitrogen-Doped Carbon Nanostructures by Combined In-Solution and On-Surface Chemistry

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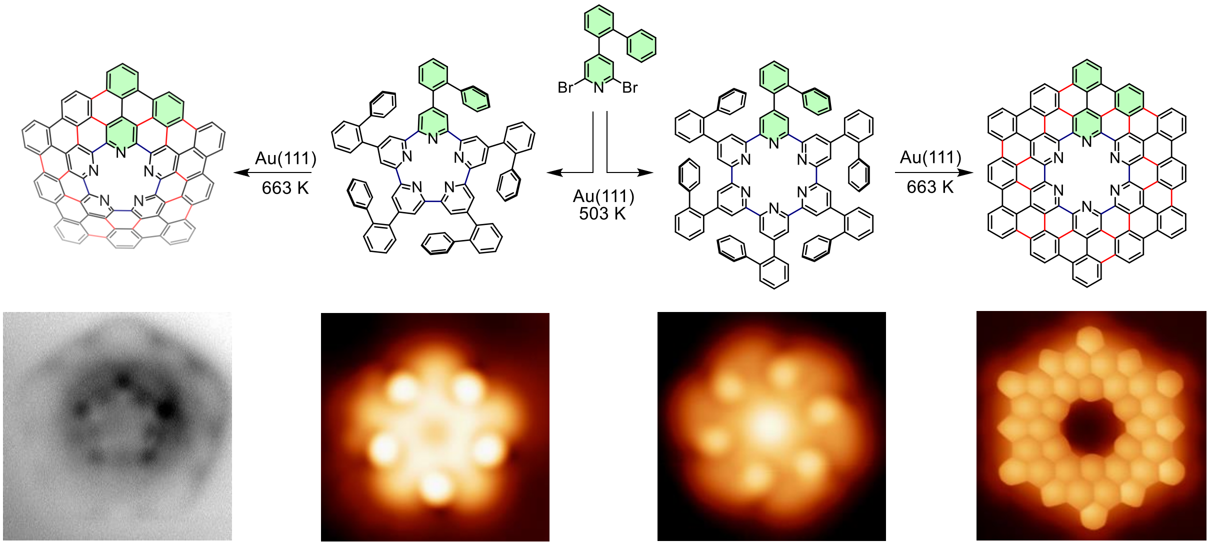
We present a combined in-solution and on-surface synthesis route to yield a variety of nitrogen-containing 0D and 1D carbon nanostructures starting from one single precursor.[1] Annealing 4-([1,1'-biphenyl]-2-yl)-2,6-dibromopyridine on a Au(111) substrate leads to Ullmann coupling followed by dehydrocyclisation to yield cycloarenes with different cavity sizes as well as a nitrogen-doped gulf-edge graphene nanoribbon. A nitrogen containing derivative of the flat C108 graphene ring[2] is formed by a ring closure of six precursor molecules. Its central cavity can host a metal atom. By filling the cavity, an energetic shift of the cycloarene's frontier orbitals is caused, where the direction of the shift depends on the metal used. A curved cycloarene (nanocone) emerges from a ring formed by five precursor molecules, whereas a higher surface coverage favours chain formation. The electronic and geometric properties of the products were investigated by scanning tunneling microscopy/spectroscopy (STM/STS) and non-contact atomic force microscopy (nc-AFM).



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# Towards the isolation of silicene quantum dots from chemical exfoliation

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Silicon is one of the most used materials in semiconductors and electronic devices [1]. Its miniaturization in two-dimensional (2D) scale presents a significant challenge aimed at enhancing and broadening its applicability in various practical domains. Layered siloxene nanosheet, a 2D silicon material with –H and –OH functional groups synthesized through the chemical exfoliation of calcium di-silicide ($CaSi_2$), have attracted a great interest in different applications such as storage energy, photocatalysis, and hydrogen evolution reaction [2-4]. However, the preparation of silicene, a 2D material composed of silicon, has not yet been achieved from $CaSi_2$, whereas numerous potential applications remain unexplored for the 2D silicon-based nanomaterials. This work introduces a novel exfoliation process for $CaSi_2$, resulting in the isolation of new 2D silicon-based nanosheets that are fully hydroxylated and contain confined silicene quantum dots. The discovery of this exotic nanomaterial opens up exciting new possibilities in various domains, with the potential for a significant impact in the 2D materials field.

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# Effect of water intercalation into tungsten trioxide structure ($WO_3.xH_2O$) (x=0,1,2): Correlation between structure and photocatalytic performance

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Tungsten oxide ($WO_3$) is a potential photoanode material for water oxidation, however, its employment is still restricted by its limited light absorption (Eg ~ 2.75 eV). A particular interest was devoted to tuning its electronic structure and optical bandgap in order to enhance its photocatalytic performance in hydrogen production as well as in advanced oxidation process. One of the promising alternatives for the enhancement of these photocatalytic performances, is the introduction of guest molecules into the tungsten oxide structure. In this paper, the photocatalytic performances of tungsten trioxide were highly improved by the intercalation of water into its structure. The intercalated compounds of chemical formula $WO_3 \cdot xH_2O$ were prepared and characterized by TGA-DSC, PXRD, FT-IR, Raman spectroscopy, SEM-EDS and XPS. The structures of intercalated materials were refined using Rietveld method and the electronic proprieties including bandgap energy, CB and VB edges were estimated using UV–visible reflectance spectroscopy. The obtained results show that the intercalation of water molecules into tungsten oxide structure reduces the gap energy of the $WO_3$ (2.4 eV) to 2.16 eV for $WO_3 \cdot H_2O$ and to 2.31 eV for $WO_3 \cdot 2H_2O$. The photocatalytic efficiency of the obtained materials was studied through oxygen evolution reaction tests in the presence of an electron acceptor ($Ag^+$) and the oxidative photodegradation of the orange G dye pollutant. We found that intercalated samples exhibit the highest efficiencies compared with anhydrous samples. These findings are correlated with the increase in the average W-O-W tilt angle in $WO_3 \cdot 2H_2O$ and $WO_3 \cdot H_2O$ compared to that of $WO_3$. This improvement in the tilt angle induces the shrinkage of the energy bandgap and increases the photocatalytic performance. Furthermore, the stability of the investigated materials was studied as a function of pH, the results reveal that the intercalation of water molecules is beneficial for the chemical stability of the hydrated tungsten oxides. These findings shed light on new alternatives for band-gap engineering and improvement of materials stability through intercalation with water molecules.

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# Synthesis and Characterization of Pentadecacene (15ac) by Tip-manipulation with a Scanning Probe Microscope

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Carbon nanomaterials exhibit versatile electronic properties that potentially can be exploited in the field of organic semiconductors. The acene series is an interesting class of compounds consisting of linearly fused polycyclic aromatic hydrocarbons (PAHs). The description as a closed-shell system becomes inadequate for long acenes as their (poly-)radical character increases. The resulting enhanced reactivity makes higher acenes hardly accessible for solution chemistry, requiring novel synthetic procedures. Here, we demonstrate the on-surface synthesis of pentadecacene (15ac), the longest acene known to date, via atom-manipulation-induced C-C-bond dissociation of a trietheno-bridged precursor on the Au(111) surface. Scanning tunneling microscopy/spectroscopy (STM/STS) and atomic force microscopy (AFM) were carried out at temperatures below 5 K to investigate the geometric and electronic properties of 15ac. It is found that 15ac has an antiferromagnetic singlet (S=0) ground state characterized by a singlet-triplet gap of 124 meV and a transport gap of 1.11 eV. Spin localization and Kondo-screening was observed for Au-complexes of 15ac with an uneven number of C-Au-bonds which reveals the S=1/2 ground state of such complexes.

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

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Starphenes are appealing compounds formed by symmetric trimerization of acenes. The potential electronic conjugation of acene arms offers starphenes distinctive physico-chemical properties, thus being promising candidates for future organic optoelectronic applications. However, due to the low solubility and instability that large starphenes present, their synthesis has been challenging. To date, the largest starphene obtained by solution-phase synthesis is [16]-starphene [1]. Herein, we propose new strategies using different molecules as precursors, obtaining a larger [19]-starphene on Au(111). Bond-resolving STM images unambiguously confirmed its chemical structure, and the density of states (DOS) of frontier molecular orbitals were resolved by dI/dV maps, further supported by density functional theory (DFT) calculations. Its multi-radical character is discussed.

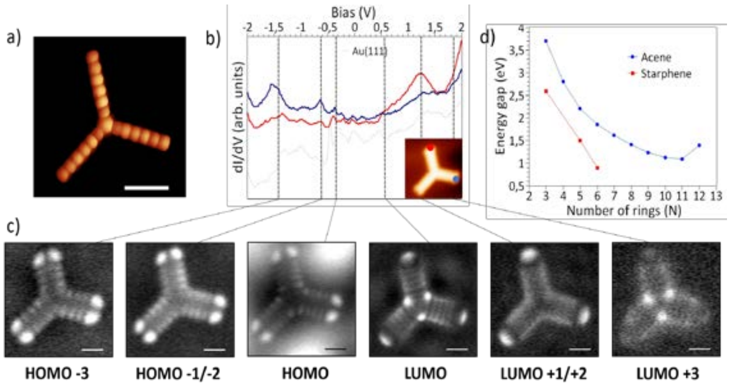

**Fig. 1**. a) BR-STM image of [19]-starphene. b) Differential conductance point spectra acquired on the molecule at the positions marked in the inset and on the bare surface. c) Conductance maps acquired at −1.42 eV, −0.64 eV, −0.36 eV, 0.54 eV, 1.2 eV and 1.85 eV. d) HOMO-LUMO gap as determined by scanning tunneling spectroscopy for starphenes and acenes of varying size. The dashed horizontal line marks the smallest acene gap reported to date, observed on undecacene.

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# How to measure cones of reaction for single-molecule collisions

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At the heart of chemistry is reagents coming together to form products. For this to occur, reagents must collide with one another in the right way. The outcome of the collision depends upon the collision energy (how hard they collide), the relative alignment of reagents (due to steric effects) and on the miss-distance between the centers of mass of the colliding species (termed the impact parameter). It has been shown that the impact parameter can be chosen for on-surface reactions by using a "surface-molecular-beam" of a $CF_2$ “projectiles” [1-2]. This beam is formed by dissociating chemisorbed $CF_3$ molecules on a Cu(110) surface with a Scanning Tunneling Microscope (STM) tip, with the projectiles being directed along the underlying rows of Cu-atoms toward a chemisorbed molecular target [1-3].

However, in these prior studies the relative alignment of the reagents before the collision was not controlled. This is addressed here through the choice of a singly-debrominated molecular target (DBTF) [4], which can adopt multiple possible adsorption alignments relative to the incoming $CF_2$ projectile. This allows collision at a selected distance from, and alignment with, the center of mass of the target which is investigated here through experiment and by theoretical calculations of barriers to reaction for different target alignments. Thus, this study demonstrates an unprecedented ability to map how collision geometry contributes to collision outcome.

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# Borazine-doped Carbon Scaffolds: From Single Molecules to 2D-BNC Architectures

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Tailor-made carbon-based molecules are commonly employed as building blocks to synthesize novel materials on surfaces, allowing structural control. When heteroatoms are incorporated into the precursor, the electronic properties of the resultant materials, e. g. graphene nanoribbons [1], 2D π-conjugated polymers [2,3] and porous covalent organic frameworks (COFs) [4] can be modified. In particular, $B_3N_3$ (borazine) substituted molecules are of great importance for the fabrication of BN-doped extended π-conjugated systems, as well as to study the effect of borazine units on the electronic structure [5].

Here, we report on the formation and low-temperature scanning tunneling microscopy / spectroscopy characterization of single BN doped molecules, amorphous BN doped carbon layer, and a BN doped COF on metal substrates by using two distinct, functionalized borazine precursors. Specifically, B,B',B''-tri[pyren-2-yl]-N,N',N''-triphenylborazine undergoes temperature-induced cyclodehydrogenation to form planarized molecules, which can further engage in dehydrogenative covalent coupling, affording amorphous BNC sheets. Furthermore, dehalogenative covalent coupling of borazine substituted TBB (1,3,5-tris(4-bromophenyl) benzene) yields a COF, featuring a band gap exceeding 4 eV.

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# STM Luminescence of Ultrathin ZnO Films on Ag(111)

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Ultrathin ZnO films on Ag(111) exhibit a layer-dependent electronic structure and conduction band edge (CBE) whose strong coupling to an interface state (IS) dominates the optical properties of the system. Previous studies combining optical excitation with scanning tunneling microscopy (STM) have shown that resonant optical excitation at the IS-CBE transition gives rise to chemical enhancement in tip-enhanced Raman spectroscopy (TERS) [1] and to enhanced photoinduced tunneling [2]. The optical enhancement thereby exhibits pronounced dependence on the local electronic structure which can vary on the nanoscale. In this work, we perform STM-luminescence (STML) spectroscopy to gain deeper insights into the local optical and electronic properties of ultrathin ZnO/Ag(111). We find that tunneling into the CB at positive sample bias gives rise to strong plasmonic luminescence at photon energies smaller than CBE onset, while higher photon energies are quenched. In contrast, STML at negative sample bias results in plasmonic luminescence as observed on bare Ag(111), excluding that dipole-coupling (re-absorption) is responsible for luminescence quenching at high photon energies. Our results show that efficient light-emitting states reside near the CBE, which serve as a bias-independent initial state for radiative plasmonic decay after elastic charge injection into the CB. The layer-dependent energetic position of the CBE thus allows the plasmonic luminescence spectra to be controlled by the ZnO film thickness.

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# On-surface molecular sensors for individual Ba tagging: application in neutrinoless double beta decay experiments

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If neutrinos are their own antiparticles, a very rare nuclear process ($T_{1/2} > 10^{26}$ yr) called neutrinoless double beta decay can occur. An unambiguous observation of such decay would open a window to answer transcendental questions beyond the physics known today, like the Universe preference for matter over antimatter or the origin of neutrino masses.

To succeed, experiments looking for these decays need to work in a highly controlled and hard-to-reach background-free regime, for which a technique called barium tagging is being developed. This technique consists in identifying the $Ba^{2+}$ daughter ion generated in $^{136}Xe$ double beta decays.

Recent studies [1,2] profit from the atomic resolution provided by STM to study molecular sensors with the expected ability to trap individual $Ba^{2+}$ ions inside a chamber of thousands of kg of Xe gas, achieving the zero-background regime that experiments need. By bringing surface science and particle physics together in this way we expect to obtain a new perspective onto the research developed by multiple groups worldwide.

In this study we present the results obtained for the molecular sensors called FBI-G2 (Fluorescence Bicolor Indicators) adsorbed on a Au(111) surface, studied by STM and STS.

Our findings are that depending on the isomer of the sensor, these molecules arrange in different geometries (see Figure 1), and that this arrangement depends in turn on the molecular coverage, which can be controlled. We also report that monomers and dimers have different electronic structures, as their HOMO-LUMO gaps differ, and so are expected to do their fluorescent behaviors. This way, monomers and dimers could be distinguished by optical fluorescence setups. Furthermore, we show that the proportion of monomers and dimers on the surface can be tuned by the deposition of ions such as $Ba^{2+}$ or $Fe^{2+}$, as these ions break dimers into monomers, thought to happen due to the chelation of the sensors by these ions. This, together with the finding that the gaps for monomers and dimers differ, allows us to prove that FBI-G2 sensors provide an effective way to detect the deposition of ions for the eventual application in single ion detection experiments.

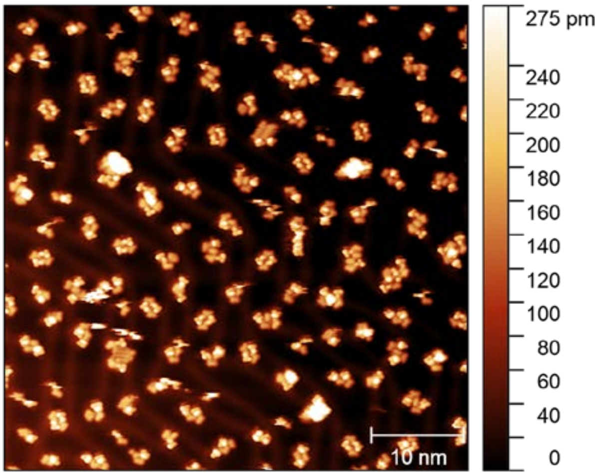

**Figure 1. STM overview, 0.12 ML of FBI-G2**

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# On Surface synthesis of a Dicaesium Tetraphenylporphyrin Complex

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Tetrapyrroles such as porphyrins and their metal complexes exhibit interesting chemical and optoelectronic properties leading to numerous potential applications in photosensor technology and organic electronics. While the surface chemistry of transition metal porphyrin complexes has been extensively studied, there is a growing interest in exploring complexes with alkali metals.[1,2] This study focuses on the on surface reaction of tetraphenylporphyrin ($H_2$(tpp)) with caesium in the multilayer and monolayer regime on Ag(111) and Au(111). The reaction product was conclusively identified by temperature programmed desorption mass spectrometry (TPD-MS) as $Cs_2$(tpp), where both aminic hydrogens were replaced by caesium ions. The data also indicate that $Cs_2$(tpp) is thermally stable up to 700 K. Upon annealing up to 400 K the N 1s X-ray photoelectron spectra revealed a complete metalation to $Cs_2$(tpp) in the monolayer, whereas in the multilayer a partial conversion is already observed at room temperature. DFT calculations indicate that $Cs_2$(tpp) exhibits a bipyramidal structure with caesium ions on both sides of the molecular plane. The conducted study sheds light on the on surface coordination chemistry of heavy alkali metal tetrapyrrole complexes potentially leading to further improvement and advancements in modern technologies.

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