

O 7: Focus Session: Functional Molecules at Surfaces I

This focus session aims at discussing motion and intramolecular changes taking place in functional molecules adsorbed at surfaces. Fundamental physical and chemical processes as for instance lateral displacement, molecular dynamics, conformational changes, or chemical reactions will be considered from the experimental and theoretical point of view. Various stimuli can be employed to induce such processes: from heat and light, which address many molecules at the same time, to the tip of a scanning probe microscope that acts locally on a single molecule.

Organizers: Francesca Moresco (TU Dresden) and Leonhard Grill (University of Graz)

Time: Monday 10:30–13:45

Location: TRE Ma

O 7.1 Mon 10:30 TRE Ma

Tuning the Halogen Bond between Adsorbed Organic Molecules — JALMAR TSCHAKERT¹, QIGANG ZHONG¹, SEBASTIAN AHLES², PASCAL HENKEL³, TOBIAS SCHLÖDER³, CARLOS ROMERO MUNIZ⁴, PABLO PUO⁴, RUBEN PEREZ⁴, DOREEN MOLLENHAUER³, HERMANN A. WEGNER², ANDRE SCHIRMEISEN¹, and •DANIEL EBELING¹ — ¹Institute of Applied Physics, Justus Liebig University Giessen, Germany — ²Institute of Organic Chemistry, Justus Liebig University Giessen, Germany — ³Institute of Physical Chemistry, Justus Liebig University Giessen, Germany — ⁴Departamento de Física Teórica de la Materia Condensada, Universidad Autónoma de Madrid, Spain

Halogen bonds are ideally suited for designing molecular assemblies because of their strong directionality and the possibility of tuning the interactions by using different types of halogens or molecular rests. This is interesting for applications in supramolecular chemistry, crystal engineering, or drug design. Here, we present a new approach for tuning the 2D self-assembly process of organic molecules by adsorption to different metal surfaces. The so-called σ -hole, the positive region at the cap of a halogen, which acts as the halogen bond donor can be actively tuned by molecule-substrate interactions. Since this effect depends strongly on the polarizability of the halogen and the reactivity of the metal substrate it can be employed for controlling intermolecular connections including their bonding angles and the selectivity of bonding sites. Our results provide new insights into the nature of halogen bonds and their complex interplay with metal surfaces.

O 7.2 Mon 10:45 TRE Ma

Giant thermal expansion triggered by alkyl chain functionalization — •SEBASTIAN SCHERB¹, ANTOINE HINAUT¹, RÉMY PAWLAK¹, GUILHERME VILHENA¹, SARA FREUND¹, ZHAO LIU¹, KLAUS MÜLLEN², THILO GLATZEL¹, AKIMITSU NARITA², and ERNST MEYER¹ — ¹Department of Physics, University of Basel, Basel, Switzerland — ²Max Planck Institute for Polymer Research, Mainz, Germany

Thermal expansion, the response in shape or size of a solid to heat, is a fundamental property governing their mechanical applicability. Due to various mechanisms involving intrinsic flexibility, conformational changes and weak intermolecular interactions, molecular architecture allows negative and large positive expansions [1]. However, understanding of the underlying mechanisms down to the molecular scale remains elusive.

Here, we investigate the influence of alkyl chain functionalization on the thermal response of molecular assemblies by non-contact AFM, STM and molecular dynamic simulations (MD) at different temperatures [2,3]. Upon heating from 5 K to 300 K the alkyl chains undergo large thermal fluctuations compared to the cores because of entropic effects and large anharmonic vibrations [3]. This results in temperature-dependent intermolecular interactions that promote a giant expansion of the networks with temperature.

[1] Liu, Z. et al. Chem. Commun. 54, 5164-5176 (2018).

[2] Hinaut et al., Nanoscale, 10, 1337-1344 (2018).

[3] Scherb, S. et al., in preparation (2019).

O 7.3 Mon 11:00 TRE Ma

On-surface assembly of supramolecular graphyne-like networks: from hydrogen- and halogen-bonded to organometallic structures — ZECHAO YANG¹, LUKAS FROMM², TIM SANDER¹, JULIAN GEBHARDT², TOBIAS A. SCHAUB³, ANDREAS GÖRLING², MILAN KIVALA³, and •SABINE MAIER¹ — ¹Department of Physics, FAU Erlangen-Nürnberg — ²Chair of Theoretical Chemistry, FAU Erlangen-Nürnberg — ³Organisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg

The on-surface assembly of graphyne-like 2D networks is directive for the long-awaited synthesis of the elusive carbon allotrope graphyne. On-surface synthesis facilitates the formation of single-layered materials, however, one of the key issues in the graphyne synthesis is the control of the alkyne coupling reaction. Here, we demonstrate a supramolecular approach to assemble highly-ordered, monolayered hydrogen-/halogen-bonded and organometallic graphyne-like 2D networks from H-/Br-functionalized triethynyltriazine derivatives on Ag(111) and Au(111). The structural and electronic properties of the supramolecular graphynes have been investigated by STM in combination with DFT. We found that intermolecular N \cdots Br-C(*sp*) halogen-bonds – hitherto unexplored in surface-supported self-assemblies – lead to significantly stronger bonded networks compared to N \cdots H-C(*sp*) hydrogen-bonds. After debromination, organometallic networks with Ag/Au-bis-acetylide bonds are formed. The highly-ordered monolayers feature unoccupied electronic states that are delocalized along the networks, which is indicative for a strong reversible bonding.

Invited Talk

O 7.4 Mon 11:15 TRE Ma

Surface templating in on-surface synthesis: Directing the reaction pathway — ANTJE KUTZ¹, MD TAIBUR RAHMAN², VILLE HAAPASILTA³, CHIARA VENTURINI⁴, RALF BECHSTEIN², ANDRÉ GOURDON⁴, ADAM S. FOSTER³, and •ANGELIKA KÜHNLE² — ¹Johannes Gutenberg University Mainz — ²Bielefeld University — ³Aalto University — ⁴CNRS, CEMES, Toulouse

On-surface synthesis constitutes a very promising strategy for creating stable functional structures on surfaces. In the past, classical reactions known from solution synthesis have been transferred onto surfaces. Due to the presence of the surface, on-surface synthesis provides the potential of directing the reaction pathway in a manner that might not be accessible in classical solution synthesis. In particular, on-surface polymerization has been discussed for creating electrical contacts in future molecular electronic devices, for which electrically insulating substrates are desired. In this talk, we present evidence for an acetylene polymerization from a terminal alkyne monomer deposited onto the (10.4) surface of the bulk insulator calcite. Moreover, the terminal alkyne forms homo-coupled dimers on the surface. Although the dimer is present, we find no indication for diacetylene polymerization. This is in sharp contrast to what is observed when directly depositing the dimers. Our work thus constitutes a demonstration for controlling the specific reaction pathway in on-surface synthesis by the presence of the surface.

O 7.5 Mon 11:45 TRE Ma

Selective on-surface synthesis of oxygen heterocycles on metals — •ANDREAS DOERR¹, NEMANJA KOCIC¹, KONSTANTIN AMSHAROV², and SABINE MAIER¹ — ¹Department of Physics, Erwin-Rommel Straße 1, 91052 Erlangen — ²Institute for Chemistry, Kurt-Mothes-Straße 2, 06099 Halle (Saale)

Heterocycles with nitrogen, oxygen, or sulfur atoms are the basic units to incorporate chemical functionalization into carbon scaffolds. For oxygen-doped nanographenes, furan[1] and pyran - having five- and six-membered rings, respectively - are the most common ones. However, their on-surface synthesis via cyclomerization reactions remains elusive so far. Here we present a low-temperature scanning tunneling microscopy study to understand the on-surface synthesis of furan and pyran derivatives from ketone-functionalized precursors on metal surfaces. We use thermally induced CH-activation reactions to fuse two ketone-derivatives in either cis- and trans-configuration selectively. Finally, cyclomerization reactions towards furan and pyran moieties are observed after further annealing. These results are highly unexpected because ketone derivatives are mostly known to convert to cyclic trimers or tetramers in solution-based chemistry. On the surface,

however, the strong interaction of the ketones with the metal surface opens up new reaction pathways.

References

[1] L. Liu, H. Klaasen, A. Timmer, H.Y. Gao, D. Barton, H. Mönig, J. Neugebauer, H. Fuchs, A. Studer: *J. Am. Chem. Soc.* 2018, 140, 18, 6000-6005

O 7.6 Mon 12:00 TRE Ma

UV-light assisted on-surface synthesis of polyphenyl chains — ●KATHRIN SCHNEIDER, JACQUES BONVOISIN, and VERONIQUE LANGLAIS — Center of Materials Elaboration and Structural Studies (CEMES) -CNRS, 29 rue Jeanne Marvig, 31055 Toulouse, France

On surface synthesis is a powerful tool to create extended molecular structures directly on a surface such as molecular chains or networks, not synthesizable in solution. In order to get a detailed understanding of the reaction steps and to optimize the reaction parameters, we studied commercial diiodo-p-ter-phenyl as model molecules.

These iodine functionalized molecules should react between them by losing their halogen and by creating C-C bonds upon Ullmann coupling. Scanning Tunneling Microscopy and Spectroscopy (STM and STS) were used to study them on Ag(001) surface, acting as substrate and catalyst. Carbon-iodine bond dissociation energy was determined by bond cleavage with the STM tip. Unreacted molecules forming a self-assembly monolayer convert, depending on annealing temperature, into organometallic and finally to fully polymerized molecular chains. The reaction temperature could clearly be reduced by using UV-light in addition to thermal treatment. These results open the route for on-surface synthesis dealing with larger or more fragile molecules.

O 7.7 Mon 12:15 TRE Ma

Free energy QM/MM simulations of on-surface reaction pathways. — ●AURELIO GALLARDO^{1,2}, ADAM MATĚJ¹, JESÚS MENDIETA-MORENO¹, and PAVEL JELÍNEK^{1,2} — ¹IOP of the Czech Academy of Sciences, Prague, Czech Republic — ²RCPTM, Olomouc, Czech Republic

On-surface chemistry represents a fast-growing field allowing to synthesize molecular structures not available by traditional wet chemistry. In combination with high-resolution scanning probe technique providing the unprecedented spatial resolution, individual products of reactions can be precisely identified. Nevertheless, a deep understanding of the reaction mechanism under the conditions imposed by the substrate remains unknown.

Widely adopted energy reaction path techniques will only describe the potential energy landscape at zero Kelvin, while the free energy landscape at given temperature enables a more appropriated description of the reaction. Such simulations including temperature effect include the effect of entropy, vibrations modes, concerted motion, etc. Consequently, such simulations avoid local minima and allows to explore different states, revealing lower energy pathways.

We will present QM/MM simulations of strain-induced isomerization in one-dimensional metal-organic chains on Cu(111) surface [1] and pp π -conjugated polymers on Au(111) surface. The simulation demonstrates the importance of the temperature effect on proper description of the reaction mechanism.

[1] M. Telychko et al., *Angew. Chem* 2019, 58

O 7.8 Mon 12:30 TRE Ma

Dynamic adaptation of linear bis-hydroxamic acid modules in complex nanostructures — ●ANTHOULA C. PAPAGEORGIOU¹, CHAO JING¹, BODONG ZHANG¹, SABINE SYNKULE¹, MARYAM EBRAHIMI¹, ALEXANDER RISS¹, WILLI AUWÄRTER¹, LI JIANG¹, GUILLAUME MÉDARD², JOACHIM REICHERT¹, and JOHANNES V. BARTH¹ — ¹Physics Department E20, Technical University of Munich, Germany — ²Chair of Proteomics and Bioanalytics, Technical University of Munich, Germany

Recently, we functionalised linear building blocks with two terminal hydroxamic acid groups and applied them to two-dimensional (2D) architectonics on the close-packed single crystal surfaces of silver and gold.¹ A combination of scanning tunnelling microscopy, atomic force microscopy, X-ray photoelectron spectroscopy and density functional theory investigations found that the molecular building block would ever so slightly adapt its shape in the environment provided by the supporting surface and its neighbouring molecules. This affords an unusual manifold of surface supramolecular motifs: two to six molecules held together by intermolecular interactions. Only a handful of these motifs organised in 2D crystals, ranging from close-packed structures to polyporous networks. Dynamic, chiral supramolecules formed enan-

tioselectively within some of the larger network pores, demonstrating chirality transfer from host to guest. Molecular coverage, as well as the chemical state of the hydroxamic acid functional group are correlated to the complex self-assembly scenario.

1) *Angew. Chem., Int. Ed.* 2019 DOI: 10.1002/anie.201912247.

O 7.9 Mon 12:45 TRE Ma

Tailoring topological order and π -conjugation to engineer quasi-metallic polymers — ●SHAYAN EDALATMANESH¹, BORJA CIRERA², ANA SÁNCHEZ-GRANDE², BRUNO DE LA TORRE^{1,3}, JOSÉ SANTOS^{2,5}, EIDER RODRÍGUEZ-SÁNCHEZ^{2,5}, KOEN LAUWAET², BENJAMIN MALLADA¹, RADEK ZBOŘIL¹, RODOLFO MIRANDA^{2,6}, OLIVER GRÖNING⁴, PAVEL JELÍNEK^{1,3}, NAZARIO MARTÍN^{2,5}, and DAVID ĚCIJA² — ¹Regional Centre of Advanced Technologies and Materials, Czechia — ²IMDEA Nanociencia, Spain — ³Institute of Physics, The Czech Academy of Sciences — ⁴EMPA, Swiss Federal Laboratories for Materials Science and Technology — ⁵Universidad Complutense, Spain — ⁶Universidad Autónoma de Madrid, Spain

Topological band theory provides a conceptual framework to predict or even engineer robust metallic states at the boundaries of topologically distinct phases. The bulk-boundary correspondence requires that a topological electronic phase transition between two insulators must proceed via closing of the electronic gap. Therefore, it can provide a conceptual solution to the instability of metallic phases in π -conjugated 1D polymers.

In this work, we demonstrated that on-surface chemical reactions of molecular precursors on pristine Au(111) surfaces result in the formation of long, defect-free, π -conjugated polymers featuring a topological non-trivial SSH quantum phase, with a very narrow bandgap due to the proximity to the point of topological transition, in-gap zero-energy edge-states and electronic transformation of the π -conjugated polymers.

O 7.10 Mon 13:00 TRE Ma

Tuning topological phase transition and pi-conjugation of 1D pentacene polymers by their length — ●HÉCTOR GONZÁLEZ-HERRERO¹, BRUNO DE LA TORRE¹, ADAM MATĚJ¹, SHAYAN EDALATMANESH¹, NAZARIO MARTÍN², DAVID ĚCIJA², and PAVEL JELÍNEK¹ — ¹Regional Centre of Advanced Technologies and Materials, Palacký University, 78371 Olomouc, Czech Republic. — ²IMDEA Nanociencia.28049, Madrid, Spain.

The recent study of ethynylene-bridged polyacene polymers has shown the possibility to tune band gap by proximity of the topological phase transition [1]. In the specific case of pentacene polymers situated near the phase transition, a small bandgap of 350 meV and the appearance of edge-states have been reported. This behavior is attributed to a topological transition from trivial to non-trivial phases. However, minimum length required for a polymer to exhibit this transition is not clear.

Theoretical analysis based on total energy DFT simulations predicts that while dimer and trimer pentacene wire adopts aromatic pi-conjugation, longer wires exhibits quinoid π -conjugation with presence of characteristic zero bias edge states. Motivated by this observation, we have grown short pentacene chains in order to study the impact of their length in the final properties of the polymer. Using STM and AFM techniques we will characterize the electronic and structural properties trying to find the key parameters for the topological phase transition to take place and benchmark the theoretical prediction.

[1] B. Cirera et al arXiv:1911.04414.

O 7.11 Mon 13:15 TRE Ma

Nanoribbons with Non-Alternant Topology from Fusion of Polyazulene: Carbon Allotropes Beyond Graphene — ●QITANG FAN¹, DANIEL MARTIN-JIMENEZ², DANIEL EBELING², CLAUDIO K. KRUG¹, LEA BRECHMANN³, CORINNA KOHLMAYER³, GERHARD HILT³, WOLFGANG HIERINGER⁴, ANDRÉ SCHIRMEISEN², and J. MICHAEL GOTTFRIED¹ — ¹Department of Chemistry, Philipps University Marburg, Germany — ²Institute of Applied Physics, Justus Liebig University Gießen, Germany — ³Institute of Chemistry, Carl von Ossietzky University Oldenburg, Germany — ⁴Department of Chemistry and Pharmacy, Friedrich-Alexander-Universität Erlangen-Nürnberg, Germany

Various two-dimensional carbon allotropes with nonalternant topologies, such as pentaheptites, have been proposed. Predictions indicate that these metastable carbon polymorphs possess unusual (opto)electronic properties. However, none of these materials has been achieved experimentally due to synthetic challenges. Here, by us-

ing on-surface synthesis, nonalternant phagraphene and tetra-penta-hepta graphene nanoribbons have been obtained by dehydrogenative C-C coupling of polyazulene chains. These chains were formed in a preceding reaction step via on-surface Ullmann coupling of 2,6-dibromoazulene. Low-temperature scanning probe microscopies with CO-functionalized tip and DFT calculations have been used to elucidate their structural properties. The proposed synthesis of nonalternant carbon nanoribbons from fusion of synthetic line defects may pave the way for the preparation of novel 2D carbon allotropes.

O 7.12 Mon 13:30 TRE Ma

CO ligation to Ru tetraphenylporphyrins on Ag(111) —

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³Chemistry Department, ENS Paris, France

For the creation of novel materials and devices, inspiration is frequently sought in nature. Porphyrin molecules are macrocyclic compounds of biological origin, which incorporate a large fraction of the chemical elements. Their versatile properties stimulated widespread application to surface functionalisation.¹ In biology, the binding of small molecules to metal centres of porphyrins determines many vital functions. For Ru tetraphenyl porphyrins (Ru-TPP), CO is determined to have an unusually high ligation energy (1.9 eV).² Here we study the effect of the porphyrin surface environment on this ligation for Ru-TPP on Ag(111). We use scanning tunnelling microscopy to find a cis-carbonyl ligation³ at low temperatures and an axial ligation at higher temperatures, which is also examined with temperature programmed desorption. We correlate the axial binding to conformational and electronic changes, investigated by density functional theory, X-ray photoemission and X-ray standing waves.

1) *Nat. Chem.* **2015**, *7*, 105; 2) *Phys. Chem. Chem. Phys.* **2018**, *20*, 11730; 3) *Nat. Chem.* **2011**, *3*, 114.