

O 6: Nanostructures at Surfaces 1

Time: Monday 10:30–13:00

Location: S052

O 6.1 Mon 10:30 S052

Autonomous non-contact molecular manipulation of nanocars based on reinforcement learning — ●BERNHARD R. RAMSAUER¹, GRANT J. SIMPSON², LEONHARD GRILL², OLIVER T. HOFMANN¹, and ANDREAS JEINDL¹ — ¹Institute of Solid State Physics, NAWI Graz, Graz University of Technology, Petersgasse 16, 8010 Graz, Austria — ²Institute of Chemistry, NAWI Graz, University Graz, Heinrichstraße 28/IV, 8010 Graz, Austria

At the world's first race of nanocars at the CEMES-CNRS, in France, participants had to direct a nanocar across a specific *racetrack* [1]. In order to control their nanocar, they have to manipulate it via an STM-tip, without being in direct contact with the nanocar. The physics that govern the molecule's movement and rotation is complex and involves the interaction between the tip and the molecule as well as the molecule and the substrate [2]. Thus, it requires time and effort for humans to be able to maneuver a molecule with a reasonable success rate. However, predicting the outcome of a performed action is unintuitive and often hard to predict for humans. Therefore, we developed an artificial intelligence (AI) based on reinforcement learning (RL) and show how it can be implemented to manipulate single molecules. The AI utilizes an off-policy learning algorithm known as Q-Learning. Our results can be the basis for more sophisticated techniques of non-contact molecular manipulations. This allows to identify and manoeuvre single molecules at will, building the basis for future bottom-up constructions of nanotechnology. [1] G. Rapenne et al., *Nature Rev. Mater.* 2, 17040 (2017) [2] G. J. Simpson et al., *Nature Nanotech.* 12, 604 (2017)

O 6.2 Mon 10:45 S052

Constructing covalent organic nanoarchitectures molecule by molecule via scanning probe manipulation — QIGANG ZHONG^{1,2}, ALEXANDER IHLE^{1,2}, SEBASTIAN AHLES^{2,3}, HERMANN A. WEGNER^{2,3}, ANDRE SCHIRMEISEN^{1,2}, and ●DANIEL EBELING^{1,2} — ¹Institute of Applied Physics, Justus Liebig University Giessen, Germany. — ²Center for Materials Research, Justus Liebig University Giessen, Germany. — ³Institute of Organic Chemistry, Justus Liebig University Giessen, Germany

Constructing low-dimensional covalent assemblies with tailored size and connectivity is challenging yet often key for applications in molecular electronics where optical and electronic properties of the quantum materials are highly structure dependent. We present a versatile approach for building such structures block by block on bilayer sodium chloride (NaCl) films on Cu(111) with the tip of an atomic force microscope, while tracking the structural changes with single-bond resolution. Covalent homo-dimers in *cis* and *trans* configurations and homo-/hetero-trimers were selectively synthesized by a sequence of dehalogenation, translational manipulation and intermolecular coupling of halogenated precursors. Further demonstrations of structural build-up include complex bonding motifs, like carbon-iodine-carbon bonds and fused carbon pentagons. This work paves the way for synthesizing elusive covalent nanoarchitectures, studying structural modifications and revealing pathways of intermolecular reactions. *Nature Chemistry* 13, 1133-1139 (2021)

O 6.3 Mon 11:00 S052

Electronic and magnetic properties of an on-surface synthesized 2D metal organic framework — ●AMINA KIMOUCHE^{1,2}, ROBERTO ROBLES³, NOEMI CONTRERAS¹, DANIEL RUIZ¹, and AITOR MUGARZA^{1,4} — ¹Institut Català de Nanociència i Nanotecnologia, Barcelona, Spain — ²Institut für Physik und Astronomie, Universität Potsdam, Potsdam, Germany — ³Centro de Física de Materiales CFM/MPC (CSIC-UPV/EHU), Donostia-San Sebastián, Spain — ⁴ICREA Institució Catalana de Recerca i Estudis Avançats, Barcelona, Spain

2D MOFs constitute a new class of designer materials where the co-existence of Dirac electrons and flat bands can lead to rich physical phenomena and to the realization of quantum phases such as topological or quantum anomalous Hall insulators.

Following the concepts of coordination chemistry, based on a surface-assisted self-assembly of the metal and organic components, we have carried out synthesis of Iron-hexaiminotriphenylene (HITP) MOFs on Au(111) substrate and characterized their electronic structure using scanning tunnelling spectroscopy (STS). On the other hand, ab-initio

calculations of the observed structures indicate the presence of strong ferromagnetic interactions that persist under the influence of the Au substrate, indicating that the interaction with the Au substrate stabilizes even further the FM state on Fe₃(HITP)₂. We relate such strong magnetic interactions to the formation of a radical spin at the ligand that mediate the inter-ionic interactions.

O 6.4 Mon 11:15 S052

Host guest chemistry and supramolecular doping in triphenylamine-based covalent frameworks on Au(111) — CHRISTIAN STEINER¹, LUKAS FROMM², JULIAN GEBHARDT², YI LIU¹, ALEXANDER HEIDENREICH², NATALIE HAMMER², ●HEXIA SHI¹, ANDREAS GÖRLING², MILAN KIVALA³, and SABINE MAIER¹ — ¹Department of Physics, Friedrich-Alexander Universität Erlangen-Nürnberg, Erlangen, Germany — ²Department of Chemistry and Pharmacy, Friedrich-Alexander Universität Erlangen-Nürnberg, Erlangen, Germany — ³Organisch-Chemisches Institut & Centre for Advanced Materials, Ruprecht-Karls-Universität Heidelberg, Heidelberg, Germany

We report the host-guest interaction in triphenylamine-based covalently-linked macrocycles and networks on Au(111) using low-temperature scanning tunneling microscopy in combination with density-functional theory. Triphenylamine precursors formed macrocycles and 2D networks featuring carbonyl- and hydrogen-functionalized pores, creating preferred adsorption sites for trimesic acid (TMA) and halogen atoms. TMA binds through hydrogen bonds to the carbonyl sites while halogens selectively adsorb between two carbonyl groups at Au hollow sites. Band structure calculations reveal that TMA adsorption reduces the electronic band gap of the triphenylamine covalent frameworks due to charge transfer, while the interaction of the halogens leads to a slight downshift of the bands.^[1]

[1] Steiner, C. et al. *Nanoscale*, 2021, 13, 9798-9807.

O 6.5 Mon 11:30 S052

Carbon-carbon coupling on inert surfaces via a radical deposition source - proof-of-concept, challenges and perspective — ●GIANLUCA GALEOTTI¹ and MARKUS LACKINGER^{1,2} — ¹Deutsches Museum, Museumsinsel 1, 80538 Munich, Germany — ²Technische Universität München, James-Frank-Str. 1, 85748 Garching, Germany

The realization of one-atom thin C-C-bonded nanostructures is an ongoing challenge of nanotechnology. Those are, however, almost exclusively synthesized on metal surfaces, taking advantage of the catalytic activity to lower the required temperature for monomer activation below the desorption threshold. The development of methods for the direct synthesis on inert and insulating surfaces would be a milestone in the field, enabling studies of nearly unperturbed covalent nanostructures with unique electronic properties, such as graphene nanoribbons and-conjugated 2D polymers. Here, we will describe the development of a Radical Deposition Source (RaDeS) for the direct deposition of radicals onto inert surfaces for subsequent coupling into C-C bonded polymers. The radicals are generated en route by indirect deposition of halogenated precursors through a heated reactive tube, where the dehalogenation reaction proceeds. As a model system for inert surfaces, we use Ag(111) passivated with a closed monolayer of chemisorbed iodine. We will first illustrate the proof-of-concept with the synthesis of poly-para-phenylene from iodinated terphenyl precursors. Subsequently, we show how this approach can be used to overcome limitations of the conventional on-surface synthesis imposed by desorption, opening additional pathways for the synthesis of nanostructures.

O 6.6 Mon 11:45 S052

Carbon-based low-dimensional materials from first principles — ●NIKLAS ENDERLEIN, ROLAND GILLEN, SABINE MAIER, and JANINA MAULTZSCH — Friedrich-Alexander-Universität Erlangen-Nürnberg

Bottom-up synthesis of carbon-based networks from molecular precursors offers a promising path to material design, where the structural, electronic, optical and vibrational properties, in principle, can be tailored through the choice of the precursor structures and functionalization. Prominent examples for this method are chevron-type graphene nanoribbons with defined topology [1] and highly controllable nitrogen incorporation [2], or multifunctional nanoporous graphene [3]. Considering the vast number of possible carbon-based networks, density

functional theory (DFT) is a powerful tool for the preselection and design of promising molecular precursors based on the computational prediction of their intrinsic physical properties.

In this spirit, we present the results of recent DFT simulations on potentially interesting carbon-based networks that lend themselves to on-surface bottom-up synthesis through Ullmann coupling of well-defined molecular precursors. We show how the electronic properties are significantly affected by the network topology and the structure of the molecular building blocks, potentially giving rise to novel phenomena. Our results inspire further efforts in the direction of molecular precursor design.

- [1] Y. Lee et al., Nano letters 18.11, 7247-7253 (2018)
- [2] C. Bronner et al., Angewandte Chemie 125.16, 4518-4521 (2013)
- [3] C. Moreno et al., Science 360.6385, 199-203 (2018)

O 6.7 Mon 12:00 S052

Covalently linked molecules as 1D materials — ●SAMUEL VASCONCELOS and MICHAEL ROHLFING — University of Münster

We performed first-principles calculations to address the problem of the formation and characterization of covalently linked structures with molecules as building blocks. We show that upon pressure a re-hybridization process takes place which leads to one-dimensional compounds resembling nanowires, in which carbon atoms are all 4-fold coordinated and possess remarkable mechanical properties. We show that for porphyrins, the resulting 1D nanostructures have metallic character. Moreover, in the case of porphyrin-metal complexes, we find that the covalently linked structures may be a platform for the stabilization of straight metallic wires. We extend the methodology for the kekulene family, that throughout the same processes forms sp³ nanotubes.

O 6.8 Mon 12:15 S052

Peierls distortion and charge density waves in novel exfoliable 1D materials — ●CHIARA CIGNARELLA¹, DAVIDE CAMPI², and NICOLA MARZARI¹ — ¹THEOS and MARVEL, EPFL, Lausanne, Switzerland — ²Universita di Milano Bicocca, Milano, Italy

One-dimensional materials are extremely attractive due to their unique electronic properties and potentialities in next-generation applications. A high-throughput screening has provided a portfolio of more than 800 novel 1D/quasi-1D materials exfoliable from the 3D Van der Waals compounds, out of which we select a dataset of metallic chains as possible candidates for vias and interconnects. Often, their low-dimensional nature leads to dynamical instabilities in the form of Peierls distortions or charge density waves (CDW), which drive structural phase transitions at finite wavevectors. Here, we analyse the stability of this novel class of materials, identifying the reconstructed stable superstructure from the phonon modes. In order to get more insight into the mechanism of the CDW, we then investigate the nesting function and the critical role of the electron-phonon coupling, still unexplored in real quasi-1D systems.

O 6.9 Mon 12:30 S052

Emulating organic molecular orbitals with artificial atoms on a surface — ●E. SIERDA, D. BADRTDINOV, B. KIRALY, E. J. KNOL, X. HUANG, M. I. KATSNELSON, G. C. GROENENBOOM, D. WEGNER, M. RÖSNER, and A. A. KHAJETOORIANS — Institute for Molecules and Materials, Radboud University, Nijmegen, The Netherlands

Bottom-up strategies to emulate the orbital structure of organic compounds is an exciting prospect, especially for molecules that are complex, unstable or hard to isolate, e.g. cyclobutadiene or triangulene. A successful implementation of such an emulator requires creating and coupling artificial atoms with multi-orbital character and possibility for orbital hybridization, on a platform that does not couple to the emulated structure. We emulate the electronic structure of planar organic molecules, using coupled, bottom-up constructed quantum dots (QDs) composed of atomic ions. We illustrate that compact clusters of ions, created via atom manipulation, exhibit a well pronounced state, localized within the semiconductor bulk band gap. For a pair of such QDs, we observe two states and identify them as bonding and anti-bonding via spatial maps. Linear chains of QDs exhibit emulated linear combinations of atomic orbitals with both s- and p-like character. Furthermore, we construct artificial structures resembling sp²-hybridized organic molecules. A rich electronic structure with pronounced states is found in tunneling spectroscopy. By comparing their spatial maps with quantum-chemical simulations of the organic compound, we can identify the states as emulated organic orbitals, providing evidence for sp² hybridization present in the artificial structures.

O 6.10 Mon 12:45 S052

Substrate-mediated polymorphism in monolayer self-assembly at liquid-solid interfaces — ●ARASH BADAMI BEHJAT¹, WOLFGANG HECKL^{1,2}, MICHAEL SCHMITTEL³, and MARKUS LACKINGER^{1,2} — ¹Technical University of Munich, James-Frank-Str. 1, 85748 Garching, Germany — ²Deutsches Museum, Museumsinsel 1, 80538 Munich, Germany — ³Universität Siegen, Adolf-Reichwein-Str. 2, 57068 Siegen, Germany

Scanning-Tunneling Microscopy (STM) studies of molecular self-assembly at liquid-solid interfaces require atomically flat, chemically inert, and electrically conductive substrates, hence are almost exclusively carried out on graphite. Here, we demonstrate that Au (111) passivated with a monolayer of chemisorbed iodine (I-Au(111)) constitutes a viable alternative for fundamental studies. By using aromatic homologues of tricarboxylic acids as a versatile model system, and by a direct comparison between graphite and I-Au (111), we experimentally study and demonstrate the decisive influence of molecule-surface interactions. We present three cases of a novel substrate-mediated polymorphism. On I-Au(111), we consistently find polymorphs with lower packing density and optimized intermolecular binding—a clear indication for diminished molecule-surface interactions. This hypothesis was corroborated by probing the monolayer's thermodynamic stability in variable temperature STM experiments.