O 68: Focus Session Molecular Nanostructures on Surfaces: On-Surface Synthesis and Single-Molecule Manipulation IV

This focus session aims to discuss recent advances in the on-surface synthesis, manipulation, characterization, and understanding of complex molecular architectures on surfaces. The interest in surface-confined molecular nanostructures emerges from their prospective applications in nanoscale (opto-) electronics, spintronics, solar cells, energy storage devices, and other fields. The bottom-up fabrication of surface-supported nanostructures can be based on molecular self-assembly utilizing non-covalent intermolecular interactions, covalent on-surface synthesis, or the direct manipulation of molecules. Molecular self-assembly usually leads to highly ordered nanostructures, controlled by non-covalent interactions, adsorbate-substrate interactions, as well as thermodynamic and kinetic factors. On-surface synthesis by covalent coupling of reactive precursors adsorbed on metallic, semiconducting, or even insulating surfaces has emerged as a powerful method that has opened new possibilities in exploring new routes towards the synthesis of complex low-dimensional nanostructures with unprecedented material properties, often via novel chemical reactions not available in conventional organic chemistry. Finally, the direct manipulation of molecules with the tip of a scanning probe microscope allows for unprecedented chemical transformations or structural modifications, as envisioned by the pioneers of nanotechnology. This focus session is intended to provide a platform for addressing current trends in these closely linked fields from various perspectives in experiment and theory.

Organized by
Sabine Wenzel (University of Marburg) and Christian Wagner (Forschungszentrum Jülich)

Time: Wednesday 15:00–17:45 Location: H24

O 68.1 Wed 15:00 H24

On-surface Synthesis of Aza-Coronoids — •Tim Naumann[1], Zilin Ruan[1], Olaf Kleykamp[1], Alix Kaczmarek[2], Linus Pohl[2], Andreas Achazi[2], Eugen Sharikow[1], Doreen Mollenhauer[2,3,4], Jörg Sundermeyer[1], and J. Michael Gottfried[1] — [1]Philipps-Universität Marburg, Hans-Meerwein-Str. 4, 35032 Marburg, Germany — [2]Justus Liebig Universität Gießen, Heinrich-Buff-Ring 17, 35392 Gießen, Germany — [3]Helmholtz-Institut für Polymere in Energieanwendungen, Lessingstr. 12-14, 07743 Jena, Germany — [4]Institut für Technische Chemie und Umweltchemie, Friedrich Schiller University Jena, Philosophenweg 7a, 07743 Jena, Germany

The properties of nanographenes can be tailored by altering the topology, introducing defect sites like vacancies, or doping with heteroatoms. Coronoids represent a versatile sub-class of the nanographenes and can be regarded as benzenoids featuring a cavity. In-solution synthesis of extended coronoids has shown to be challenging due to their low solubility. To gain access to various aza-coronoids, we combined in-solution and on-surface techniques. By modification of the precursor's substituents, the edge termination of the coronoids is controlled. Besides planar armchair-edge and zigzag-edge terminated coronoids, a curved coronoid was synthesized. Nitrogen functionalization of the cavity allows for hosting a metal atom, giving rise to the formation of coronoid-metal complexes. The electronic and geometric properties of the nanostructures were investigated by low temperature scanning tunneling microscopy/spectroscopy (STM/STS) and non-contact atomic force microscopy (nc-AFM) and supported by DFT calculations.

O 68.2 Wed 15:15 H24

Sequential on-surface synthesis of planar and curved fused anthracenyl-porphyrins — •Miloš Baljozović[1], Joffrey Pijeat[2], Stéphane Campidelli[2], and Karl-Heinz Ernst[1,3,4] — [1]Empa, Dübendorf, Switzerland — [2]Université Paris-Saclay, CEA, Gif-sur-Yvette, France — [3]University of Zürich, Zürich, Switzerland — [4]The Czech Academy of Sciences, Prague, Czech Republic

On-surface synthesis has lately provided means for C-C bond formation that would otherwise hardly be accessible by conventional solution chemistry. Porphyrins are of particular interest in this regard, due to the ability to fine tune their physical and chemical properties via central metal incorporation or peripheral functionalization. Nevertheless, the formation of π-extended porphyrins bearing unsubstituted anthracenyl moieties was so far not achieved.

In this contribution we demonstrate temperature controlled (cyclo)dehydrogenation of bis- and tetra-anthracenyl Zn(II) porphyrins on a Au(111) substrate. Notably, on-surface dehydrogenation is not limited to the first dehydrogenation step involving fusion of anthracenyl units to the macrocycle. Sequential dehydrogenation with temperature elevation is leading to novel planar and curved porphyrin products beyond ones obtained by wet synthesis that could be identified in our combined STM, XPS and ToF-SIMS study.[1]

Support by Swiss National Science Foundation and University of Zürich Research Priority Program LightChEC is gratefully acknowledged.

[1] Baljozović, M. et al. J. Am. Chem. Soc. - just accepted.

O 68.3 Wed 15:30 H24

On-surface synthesis of porphyrin-capped carbon nanocones — Nemanja Kocic[1], Andreas Dörr[1], Moritz Villmow[1], Kevin Dhamo[2], Michael Ruppel[2], Norbert Jux[2], Bernd Meyer[2], and •Sabine Maier[1] — [1]Department of Physics, Friedrich-Alexander-Universität Erlangen-Nürnberg, Germany — [2]Department of Chemistry and Pharmacy, Friedrich-Alexander-Universität Erlangen-Nürnberg, Germany

We demonstrate the surface-assisted transformation of porphyrin-based precursor molecules into bowl-shaped nanographenes through cyclization reactions on an Au(111) surface. The structures are visualized by scanning probe techniques with submolecular resolution, directly revealing intramolecular bonding and compared to density-functional theory calculations. Distinct configurations that suggest bowl-to-dome inversion are identified on the surface. Additionally, we report the accompanying metallation of the macrocycle with Au substrate adatoms. This combination of porphyrin and nanographene with a periphery solely consisting of six-membered all-carbon rings might serve as a seed for growing porphyrin-doped graphene sheets.

O 68.4 Wed 15:45 H24

Relating Radical Delocalization, Charge Transfer and Magnetic Ground State in Open-Shell Molecules — Tao Wang[1], Sergio Salaverria[2], Fernando Aguilar-Galindo[3], Javier Besteiro-Saez[4], Luis M. Mateo[4], Paula Angulo-Portugal[5], Jonathan Rodriguez-Fernandez[6], Dolores Perez[4], Martina Corso[1,5], Diego Peña[4], and •Dimas G. de Oteyza[1,2] — [1]Donostia International Physics Center, San Sebastián, Spain — [2]Nanomaterials and Nanotechnology Research Center (CINN), El Entrego, Spain — [3]Universidad Autónoma de Madrid, Madrid, Spain — [4]CiQUS, Santiago de Compostela, Spain — [5]Centro de Fisica de Materiales, San Sebastián, Spain — [6]University of Oviedo, Oviedo, Spain

At the same time as our capabilities to synthesize open-shell carbon-based materials are rapidly growing with the development of on-surface synthesis under vacuum conditions, the interest in pi-magnetism is rising due to its excellent prospects for potential applications. As a result, increasing efforts are being focused on the detailed understanding of open-shell carbon nanostructures and all the parameters that determine their spin densities and magnetic ground states. Here we present a facile route to synthesize different open-shell acene derivatives with closely related structures. A systematic comparison allows us to draw conclusions on the role of the functional groups, their number and distribution, as well as on the role of the radical state delocalization in relation with the presence or absence of charge transfer at interfaces, which consequently impacts the molecules pi-magnetism.

O 68.5 Wed 16:00 H24

A route toward the on-surface synthesis of organic ferromagnetic quantum spin chains — •Fabian Paschke[1], Ricardo Ortiz[2], Shantanu Mishra[1], Manuel Vilas-Varela[3], Florian Albrecht[1], Diego Peña[3], Manuel Melle-Franco[2], and Leo Gross[1] — [1]IBM Research Europe - Zurich, 8803 Rueschlikon, Switzerland — [2]CICECO - Instituto de Materiais de Aveiro, 3810-193 Aveiro, Portugal — [3]CiQUS and Department of Organic Chemistry, 15782 Santiago de Compostela, Spain

Engineering a sublattice imbalance is an intuitive way to induce high-spin ground states in bipartite polycyclic conjugated hydrocarbons. Such high-spin molecules can be employed as building blocks of quantum spin chains, which are outstanding platforms to study many-body physics and fundamental models in quantum magnetism [1].

In contrast to antiferromagnetism, demonstration of ferromagnetic coupling between polycyclic conjugated hydrocarbons has been scarce. Here, we demonstrate the on-surface synthesis of short ferromagnetic spin chains based on dibenzotriangulene, a polycyclic conjugated hydrocarbon with a triplet ground state. We achieve a direct majority-minority sublattice coupling between adjacent units, which leads to a global sublattice imbalance in the chains and therefore a ferromagnetic ground state with a strong intermolecular ferromagnetic exchange. By means of scanning probe measurements and quantum chemistry calculations, we confirm quintet and septet ground states in dimers and trimers, respectively.

[1] S. Mishra et al., Nature 598, 287 (2021).

O 68.6 Wed 16:15 H24

Atomically Precise Control of Topological State Hybridization in Conjugated Polymers — Alejandro Jiménez-Martín[1,2], Zdenka Sosnová[2], Diego Soler[2], Benjamin Mallada[1], Héctor González-Herrero[1], Shayan Edalatmanesh[1,2], Pavel Jelínek[1,2], and •Bruno de la Torre[1,3] — [1]Regional Centre of Advanced Technologies and Materials, Czech Advanced Technology and Research Institute (CATRIN), Palacký University, 78371 Olomouc, Czech Republic — [2]Institute of Physics of the Czech Academy of Sciences, 16200 Prague, Czech Republic — [3]Nanomaterials and Nanotechnology Research Center (CINN), CSIC-UNIOVI-PA, 33940 El Entrego, Spain

Realization of topological quantum states in carbon nanostructures has recently emerged as a promising platform for hosting highly coherent and controllable quantum dot spin qubits. However, their adjustable manipulation remains elusive. Here, we report the atomically accurate control of the hybridization level of topologically protected quantum edge states emerging from topological interfaces in bottom-up-fabricated π-conjugated polymers. Our investigation employed a combination of low-temperature scanning tunneling microscopy and spectroscopy, along with high-resolution atomic force microscopy, to effectively modify the hybridization level of neighboring edge states by the selective dehydrogenation reaction of molecular units in a pentacene-based polymer and demonstrate their reversible character.

O 68.7 Wed 16:30 H24

On-surface encapsulation of azafullerene radicals: towards 2D spin networks — •Marion A. van Midden Mavrič[1], Bastien Anézo[1,2], Gregor Kladnik[3,4], Luca Schio[4], Gregor Bavdek[4,5], Yuri Tanuma[1,6], Ruben Canton-Vitoria[7], Ioanna K. Sideri[7], Nikos Tagmatarchis[7], Jannis Volkmann[8,9], Herman A. Wegner[8,9], Andrea Goldoni[10], Chris Ewels[2], Alberto Morgante[4,11], Luca Floreano[4], Erik Zupanič[1], Dean Cvetko[1,3,4], and Denis Arčon[1,3] — [1]Jožef Stefan Institute, Ljubljana, Slovenia — [2]IMN, Nantes University, France — [3]FMF, University of Ljubljana, Slovenia — [4]CNR-IOM, Trieste, Italy — [5]PF, University of Ljubljana, Slovenia — [6]CAREM, Hokkaido University, Sapporo, Japan — [7]T.P.C.I., Athens, Greece — [8]Center for Materials research, Giessen, Germany — [9]Justus Liebig University, Giessen, Germany — [10]Elettra Sincrotrone Trieste S.C.p.A., Italy — [11]Phys. dept., University of Trieste, Italy

While organic radicals on surfaces are a promising platform for realizing and controlling qubits, they are usually highly reactive. Here we present on-surface encapsulation of azafullerene $C_{59}N^\bullet$ into [10]cycloparaphenylene ([10]CPP) nanohoops on Au(111) as an efficient strategy to form supramolecular complexes with long-term spin protection. By vacuum depositing $C_{59}N^\bullet$ on a pre-deposited template layer of [10]CPP, extended networks of spin 1/2 radicals in a hexagonal lattice are formed. We find compelling evidence for electronic coupling between both molecular species, show that [10]CPP protects $C_{59}N^\bullet$ against dimerization and inhibits coupling to the Au(111) substrate.

O 68.8 Wed 16:45 H24

Remote debromination on ultrathin insulating film — •Tzu-Chao Hung[1], Lucía Gómez-Rodrigo[2], Lennart Moritz[1], Manuel Vilas-Varela[2], Leo Gross[3], Diego Peña[2], and Jascha Repp[1] — [1]Institute of Experimental and Applied Physics, University of Regensburg, Germany — [2]Centro Singular de Investigación en Química Biolóxica e Materiais Moleculares (CiQUS) and Departamento de Química Orgánica, Universidade de Santiago de Compostela, Spain — [3]IBM Research Europe, Zurich, Switzerland

Open-shell carbon-based structures are widely studied in recent years not only owing to their potential applications in spintronics and as quantum devices, but they can also serve as a platform to investigate electron-correlation phenomena. One way to study open-shell molecules despite their large reactivity, is to create them from a suitable precursor in a scanning probe microscope (SPM) under ultra-high-vacuum and low-temperature conditions. Here, we demonstrate a particularly efficient debromination reaction resulting in an open-shell molecule by means of SPM manipulation on ultrathin NaCl film on Cu(111). The debromination even works remotely with the tip being up to ~10 nm away from the molecule for both voltage polarities. Based on our observation, possible reaction mechanisms will be discussed.

Invited Talk O 68.9 Wed 17:00 H24

On-Surface Synthesis of Porphyrins and BN-Substituted Carbon Scaffolds — •Willi Auwärter — Technical University of Munich, Garching, Germany

On-surface synthesis protocols provide elegant routes to individual molecular complexes, oligomers, and other carbon-based nanomaterials on metal supports [1]. The resulting structural, physical, and chemical properties can be controlled by heteroatom-substitution. The talk will report on our activities employing thermally induced reactions on coinage metal surfaces, affording heteroatom-doped porphyrins and BN-substituted carbon scaffolds. Specifically, a route to peripherally O-doped porphyrins is addressed [2]. Furthermore, we will discuss the use of functionalized borazine precursors yielding covalent carbon networks with $(BN)_3$ motifs. These include random sheet-like BNC structures [3], which can be transferred to Si waver dices, and covalent organic frameworks (COFs) on Ag(111) and Au(111). The comprehensive characterization by scanning probe microscopy, complemented by theoretical modelling, reveals that COFs with distinct $(BN)_3$ densities, pore sizes, and electronic structures can be achieved. The findings open pathways to new O- and BN-substituted carbon-based nanoarchitectures on surfaces. [1] Grill, L.; Hecht S. Nat. Chem. 12, 115 (2020). [2] Deyerling, J. et al. Angew. Chem. Int. Ed., e202412978 (2024). [3] Tömekce et al., Chem. Eur. J., e202402492 (2024).

O 68.10 Wed 17:30 H24

An electrically controlled molecular spin switch — •Kwan Ho Au-Yeung[1], Wantong Huang[1], Paul Greule[1], Máté Stark[1], Christoph Sürgers[1], Wolfgang Wernsdorfer[1], Roberto Robles[2], Nicolas Lorente[2,3], and Philip Willke[1] — [1]Physikalisches Institut, Karlsruhe Institute of Technology, Karlsruhe, Germany — [2]Centro de Física de Materiales CFM/MPC (CSIC-UPV/EHU), 20018 Donostia-San Sebastián, Spain — [3]Donostia International Physics Center, 20018 Donostia-San Sebastián, Spain

Precise control of spin states and spin-spin interactions in atomic-scale molecular complexes is key to developing multi-spin systems on surfaces for instance for applications in quantum technologies. This has been realized in a variety of systems, for instance in spin-crossover molecules. In this study, we explore the spin coupling and tunability of molecular dimer complexes on an insulating magnesium oxide film: When brought close to a single Fe adatom, a FePc molecule interacts with the Fe forming an interacting spin system. The calculated adsorption geometries by density functional theory (DFT) shed light on the two adsorption configurations of the two bistable states. The two states of the Fe-FePc complex can be successfully and reversibly switched using STM voltage pulses. Subsequently, by using scanning tunneling spectroscopy, we show that this is accompanied by an alteration of the total spin state and spin coupling in the complex. We further illustrate how the complex can be used to shift the resonance frequency of a nearby FePc in single spin resonance experiments, which demonstrates that this complex can function as a magnetic spin switch.