O 11: Focus Session: Molecular Nanostructures on surfaces - New Concepts towards Complex Architectures I

This focus session aims at covering recent progress in both the formation and understanding of complex molecular architectures on surfaces. The bottom-up fabrication of surface-supported molecular architectures is either based on molecular self-assembly utilizing non-covalent intermolecular interactions or covalent on-surface synthesis. The intention is to provide a platform for discussing important aspects of molecular ensembles in contact with metallic, semi-conducting, and insulating substrates. In the focus are recent advances in theory as well as experiments dealing with single molecule chemistry, the understanding and controlled growth of complex molecular self assemblies and on surface synthesis of covalent structures.

Organizers: Sabine Maier, FAU Erlangen-Nürnberg; Meike Stöhr, University of Groningen

Time: Monday 15:00–18:15 Location: MA 004

Invited Talk O 11.1 Mon 15:00 MA 004

Elementary phenomena in hybrid graphene nanoribbons on surfaces — •Nacho Pascual — CIC nanoGUNE, San Sebastian (Basque Country)

Graphene nanoribbons (GNR) are cornerstone materials for functional devices, but their properties strongly depend on atomic-scale details of their structure. On-surface synthesis strategies can produce them on a metal surface and control their shape with atomic precision by clever selection of organic precursors [1]. The physics of these carbon structures is full of elementary phenomenology that can be accessed with great detail combining high-resolution STM imaging with local spectroscopy. These ribbons behave as one-dimensional semiconductors with band structure that depends on their width [2] and growth direction [3], and can be tuned by doping them with chemical groups at their edge [4]. The functional character of the ribbons is enhanced when two or more precursors are mixed into hybrid ribbons, resulting in, for example, quantum electron boxes [5] embedded in the carbon backbone. To date, magnetism has been elusive in GNR structures. By incorporating magnetic species in the synthesis steps we created hybrid porphyrin-GNR molecular devices. We show that the molecular spin survives in the ribbon by using spin-excitation inelastic spectroscopy. [1] K. Cai et al., Nature 466, 470 (2010) [2] N. Merino et al., ACS nano 11, 11661 (2017) [3] D.G. de Oteyza et al., ACS Nano 10, 9000 (2016) [4] E.Carbonell et al., ACS Nano 11, 7355 (2017) [5] E. Carbonell et al., Nano Letters 17, 50 (2017)

O 11.2 Mon 15:30 MA 004

Hierarchical On-Surface Synthesis of Deterministic Graphene Nanoribbon Heterojunctions — •Christopher Bronner[1], Rebecca A. Durr[2], Daniel J. Rizzo[1], Yea-Lee Lee[1,3], Tomas Marangoni[2], Alin Miksi Kalayjian[2], Henry Rodriguez[1], William Zhao[1], Steven G. Louie[1,4], Felix R. Fischer[2,4,5], and Michael F. Crommie[1,4,5] — [1]Dept. of Physics, University of California, Berkeley, United States — [2]Dept. of Chemistry, University of California, Berkeley, United States — [3]Dept. of Physics, Pohang University of Science and Technology, Korea — [4]Materials Sciences Division, Lawrence Berkeley National Laboratory, United States — [5]Kavli ENSI, Berkeley, United States

Heterojunctions of two dissimilar bottom-up fabricated graphene nanoribbons (GNRs) provide a platform for new functional devices on the molecular scale. Their on-surface synthesis via copolymerization of two different Br-substituted precursors has been previously reported, but unselective copolymerization results in random sequences of the two constituting GNRs. We demonstrate on-surface synthesis of non-random GNR heterojunctions employing a hierarchical growth strategy. Using both I and Br-substituted precursors with different halogen bond strengths as well as a bifunctional linker molecule allows us to grow the two different segments sequentially. The resulting block-copolymers translate into deterministic GNR heterostructures of two chevron-GNRs joined in only one heterojunction, suitable for device integration.

O 11.3 Mon 15:45 MA 004

Edge states in chiral-shaped graphene nanoribbons. — •Néstor Merino-Díez[1,2], Jingcheng Li[2,3], Aran García-Lekue[1,4], Sofía Sanz[1], Thomas Frederiksen[1], Diego Peña[5], Dimas G. de Oteyza[1,4], and Jose Ignacio Pascual[2,4] — [1]Donostia International Physics Center (DIPC) , 20018 San Sebastián (Spain) — [2]CIC Nanogune, 20018 San Sebastián (Spain) — [3]Centro de Física de Materiales (CFM), 20018 San Sebastián, (Spain) — [4]Ikerbasque, 48013 Bilbao (Spain) — [5]Centro de Investigación Química Biolóxica e Materiais Meloculares (CIQUS), 15782 Santiago de Compostela (Spain)

Understanding the configuration of electrons in graphene nanoribbons (GNRs), and the physical phenomena beneath, is still a challenging quest. Among all the GNRs studied to date, chiral-shaped GNRs (i.e. with periodically alternating armchair and zigzag-like segments) represent the most scarcely explored ones.

Recently we reported the growth of narrow chiral GNRs (alternating 3 zigzag-1 armchair segments) by depositing pre-designed molecular precursors on different coinage metallic surfaces [D.G. de Oteyza et al., ACSnano 10, 9000-9008 (2016)]. This ribbon presents a small semiconducting gap of 670mV [N. Merino-Díez et al., arXiv: 1710.05813]. Here we present the on-surface synthesis of wider chiral GNRs by using molecular precursors with additional anthracene units. Using scanning tunnelling spectroscopy we demonstrate that the width strongly determines the formation and shape of electronic edges states.

O 11.4 Mon 16:00 MA 004

Topological modifications in graphene nanostructures — •Shantanu Mishra, Carlo A. Pignedoli, Pascal Ruffieux, and Roman Fasel — Empa - Swiss Federal Laboratories for Materials Science and Technology, 8600 Dübendorf, Switzerland

Graphene is the first two-dimensional crystal discovered in nature. The interesting properties of graphene arise from the sp2-network of carbon atoms and a perfect arrangement of hexagonal rings. Like any other crystal, presence of defects disrupting the pristine topology should significantly impact the physical properties of graphene. Introduction of defects thus provides a platform to tailor intrinsic properties of graphene and mandates a rational approach to achieve atomic-scale control over construction and implementation of defects for device applications. Regarding this, on-surface Ullmann reaction has become an indispensable synthetic tool to achieve atomically precise synthesis of nanostructures.

Utilizing this synthetic procedure, we fabricate two novel graphene nanostructures. The first is a non-alternant polyaromatic hydrocarbon demonstrating the first rational synthesis of the inverse Stone-Thrower-Wales defect in graphene. The second structure constitutes an organic polymer with precise substitution of specific carbon atoms with nitrogen atoms, that presents a model case for doping of graphene nanostructures with possible introduction of magnetism. Using a combined scanning tunneling microscopy and density functional theory based study, we investigate the novel properties that these altered bond or atomic topologies impart to nanographenes.

O 11.5 Mon 16:15 MA 004

Electronic band structure of poly (meta-phenylene) zigzag chains — •Ignacio Piquero-Zulaica[1], Aran García-Lekue[2,3], Claudio K. Krug[4], J. Enrique Ortega[1,2,5], J. Michael Gottfried[4], and Jorge Lobo-Checa[6,7] — [1]Centro de Física de Materiales CSIC/UPV-EHU, San Sebastian, Spain — [2]Donostia International Physics Center, San Sebastian, Spain — [3]Ikerbasque, Basque Foundation for Science, Bilbao, Spain — [4]Fachbereich Chemie, Philipps-Universität Marburg, Germany — [5]Universidad del País Vasco, Dpto. Física Aplicada I, San Sebastian, Spain — [6]Instituto de Ciencia de Materiales de Aragón (ICMA), CSIC-Universidad de Zaragoza, Spain — [7]Departamento de Física de la Materia Condensada, Universidad de Zaragoza, Spain

Carbon based low-dimenional nanostructures such as on-surface synthesized Graphene nanoribbons (GNRs) and oligophenylene chains provide a vast playground for developing organic semiconductors with specific electronic properties. For instance, recent ARPES band structure studies on macroscopically aligned poly (para-phenylene) (PPP) and armchair-GNRs unraveled highly dispersive electronic bands with a large HOMO-LUMO gap. Analogously, we generate atomically precise and aligned on-surface synthesized poly (meta-phenylene) (PMP) zigzag chains on a curved Ag(111) surface. With the use of ARPES, we unravel its band structure for the first time and find weakly dispersive bands with considerably increased HOMO-LUMO gap. These results, supported with DFT calculations, suggest a strong tunability of the polymer's electronic properties that we can correlate to its topology.

15 min. break

O 11.6 Mon 16:45 MA 004

DFT study of super-atom states in graphene nanoribbons — •Bernhard Kretz[1] and Aran Garcia-Lekue[1,2] — [1]Donostia International Physics Center (DIPC), Paseo Manuel de Lardizabal 4, E-20018 San Sebastian, Spain — [2]IKERBASQUE, Basque Foundation for Science, E-48013 Bilbao, Spain

In the two dimensional plane of graphene image states exist in the vacuum region above and below the graphene layer.[1] Such states do not follow the atomic lattice modulation and behave as nearly-free electrons (NFE). When graphene is rolled into nanotubes or fullerenes, these states overlap giving rise to the emergence of 1D NFE bands or 0D Super-Atom Molecular Orbitals (SAMOs).[2,3] In this work, we analyze a similar scenario in a reduced dimension, when the extended image states are related to the 1D edge of graphene. Using density functional theory (DFT), we investigate the emergence of 1D-NFE states in graphene nanoribbons, and we propose a way to confine them by modulating the width of the ribbons periodically, thus effectively creating 0D-SAMOs. Interestingly, the existence of a related SAMO state in the central empty region of a carbon-based macromolecule has been recently reported.[4]

[1] V. M. Silkin, et al., Phys. Rev. B, 80, 121408(R), 2009
[2] S. Hu et al., Nano Lett. 10, 4830 (2010)
[3] M. Feng et al., Science, 320, 359-362, 2008
[4] J. Heuille et al. (submitted)

O 11.7 Mon 17:00 MA 004

Precise mono-selective aromatic C-H activation by chemisorption of meta-aryne on a metal surface — •Qitang Fan[1], Simon Werner[1], Jalmar Tschakert[2], Daniel Ebeling[2], André Schirmeisen[2], Wolfgang Hieringer[3], and J. Michael Gottfried[1] — [1]Fachbereich Chemie, Philipps-Universität Marburg, Germany — [2]Institute of Applied Physics (IAP), Justus Liebig University Gießen, Germany — [3]Lehrstuhl für Theoretische Chemie, Friedrich-Alexander-Universität Erlangen-Nürnberg, Germany

Aromatic C-H activation has attracted much attention due to their wide range of applications in the synthesis of aryl-containing chemicals. The major challenge lies in the minimization of the activation barrier and maximization of the regioselectivity. Here, we report the Cu(111) surface-catalyzed highly-selective activation of the C-H bond between two meta-substituted C-Br groups anchored on a phenyl ring. Two prototype molecules, i.e., 4',6'-dibromo-meta-terphenyl and 3',5'-dibromo-ortho-terphenyl have been employed to perform reactions on Cu(111). The chemical structures of the resulted products have been clarified by the combination of scanning tunneling microscopy and non-contact atomic force microscopy. Both of them demonstrate a remarkable weakening of the C-H bond between the two C-Br groups. Density function theory reveals that this efficient C-H activation stems from the extraordinary chemisorption of the meta-aryne, which leads to the close proximity of the targeted C-H bond to the Cu(111) surface and the out-of-plane deformation of the phenyl ring. These findings pave the way for new types of C-H activation approaches.

O 11.8 Mon 17:15 MA 004

A novel surface-catalytic reaction studied by scanning probe microscopy — •Lacheng Liu[1,2], Hong-Ying Gao[1,2], Henning Klaasen[3], Alexander Timmer[1,2], Harry Mönig[1,2], Armido Studer[3], and Harald Fuchs[1,2] — [1]Center for Nanotechnology, Heisenbergstraße 11, 48149 Münster, Germany — [2]Physikalisches Institut, Westfälische Wilhelms-Universität Münster, Wilhelm-Klemm-Straße 10, 48149 Münster, Germany — [3]Organisch-Chemisches Institut and Center for Mutiscale Theory and Simulation, Westfälische Wilhelms-Universität Münster, Corrensstraße 40, 48149 Münster, Germany

On-surface synthesis is a promising surface-assisted approach to form novel functional nanostructures via covalent interaction between organic molecules. In this work, we report a novel surface-catalytic reaction on Au(111), Cu(111) and Ag(111) surfaces with the same organic molecule as precursors. The scanning tunneling microscopy (STM) imaging study shows that two different 1D covalent polymers will be formed on metal surfaces via two steps of thermal annealing, respectively. The polymerization occurs at lower thermal annealing temperature on Cu(111) than that of on Au(111) and Ag(111). To understand the pass way of the reaction on metal surfaces, non-contact atomic force microscopy (nc-AFM) and X-ray photoelectron spectroscopy (XPS) measurements were performed combined with DFT calculation. The novel reaction provides a promising way to synthesis 1D polymers on metal surfaces.

O 11.9 Mon 17:30 MA 004

On-surface synthesis of indenofluorene polymers using methyl groups to form 5-membered rings — •Marco Di Giovannantonio[1], José I. Urgel[1], Aliaksandr Yakutovich[1], Jan Wilhelm[2], Uliana Beser[3], Akimitsu Narita[3], Carlo A. Pignedoli[1], Pascal Ruffieux[1], Klaus Müllen[3], and Roman Fasel[1,4] — [1]Empa - Swiss Federal Laboratories for Materials Science and Technology, nanotech@surfaces Laboratory, 8600 Dübendorf, Switzerland — [2]University of Zurich, Department of Chemistry, 8057 Zurich, Switzerland — [3]Max Planck Institute for Polymer Research, 55128 Mainz, Germany — [4]Department of Chemistry and Biochemistry, University of Bern, 3012 Bern, Switzerland

On-surface synthesis has opened pathways to molecular nanostructures that have been inaccessible so far. Here, we show the surface-assisted aryl-aryl coupling of brominated precursor molecules, followed by the cyclization of methyl groups on a poly(para-phenylene) backbone to form 5-membered rings, and to realize a fully conjugated chain composed of indenofluorene units. Indenofluorenes are appealing molecules consisting of an array of fused 6-5-6-5-6-membered rings with 20 π-electrons, which have received increasing attention for their formal anti-aromaticity, open-shell biradical character, and narrow HOMO-LUMO gap. The structure and electronic properties of the obtained indenofluorene polymers have been characterized by STM, nc-AFM, and STS, which are supported by theoretical calculations. The reported synthetic protocol can potentially be extended to other novel molecular nanostructures to fine tune their electronic properties.

O 11.10 Mon 17:45 MA 004

On-surface formation of cumulene by dehalogenative homocoupling — Bay Tran[1], Qiang Sun[2], •Mihaela Enache[1], Liangliang Cai[2], Honghong Ma[2], Xin Yu[2], Chunxue Yuan[2], and Meike Stöhr[1] — [1]Zernike Institute for Advanced Materials, University of Groningen, Groningen, Netherlands — [2]Interdisciplinary Materials Research Center, Tongji University, Shanghai, China

Recently, on-surface synthesis based on the use of covalent linking has offered an excellent platform to construct novel 1D and 2D carbon-based materials. In particular, the thermally induced dehalogenation of pre-defined C-X groups (X = halogen) provides an efficient route to produce radicals for subsequent C-C couplings on the surface [1]. Until now, all employed halide precursors had only one halogen attached to a carbon atom. It is thus of interest to study the effect of attaching more than one halogen atom to a carbon atom with the aim of producing multiple unpaired electrons.

Herein, by introducing an alkenyl gem-dibromide, cumulene products were fabricated on an Au(111) surface by dehalogenative homocoupling reactions [2]. The reaction products and pathways were unambiguously characterized by the combination of high-resolution scanning tunneling microscopy (STM) and non-contact atomic force microscopy (nc-AFM) measurements together with density functional theory (DFT) calculations.

[1] B.V. Tran et al., Nanoscale, DOI : 10.1039/C7NR06187K
[2]Q. Sun et al., Angew. Chem. Int. Ed. 56, 12165-12169 (2017).

O 11.11 Mon 18:00 MA 004

Self-assembly and on-surface reaction of bromo-substituted decacyclene on Ag(111) — •Shadi Sorayya[1], Sachin Menon[1], Jörg Tomada[2], Konstantin Amsharov[2], and Sabine Maier[1] — [1]Department of Physics, FAU Erlangen-Nürnberg — [2]Department of Chemistry and Pharmacy, FAU Erlangen-Nürnberg

Controlling and understanding the self-assembly of chiral molecular building blocks on surfaces is essential for chiral separation and recognition. Here, we report on the self-assembly and on-surface reaction of chiral bromo-substituted decacyclene molecules adsorbed on Ag(111) using high-resolution scanning tunneling microscopy at low temperatures. The steric repulsion between adjacent hydrogen atoms at the peripheral naphthalene units of the decacyclene derivative leads to a twist in the molecular scaffold, and hence several chiral conformers are found upon adsorption on the surface. We observe compact and porous organo-metallic networks upon annealing because of the complex interplay between intermolecular forces and chirality of the constituent molecules. The structural properties of the networks and the chirality will be discussed in detail. Interestingly, we see a transition from homochiral to heterochiral networks upon annealing.