

O 103: Poster Session VIII: Surface reactions II

Time: Thursday 13:30–15:30

Location: P

O 103.1 Thu 13:30 P

Enhancement of homochirality in on-surface designed indenofluorene polymers — ●CRISTINA MARTÍN FUENTES, JOSE IGNACIO URGEL, JOSE MARIA GALLEGO, JOSE SANTOS, RODOLFO MIRANDA, NAZARIO MARTÍN, and DAVID ÉCIJA — IMDEA nanociencia, Cantoblanco 28049, Madrid, Spain

A crucial aspect in polymer science is to find out route to enhance homochirality when the monomer precursor is chiral or prochiral.

Inspired by our recent results regarding the homocoupling of acene species exploiting the =CBr² functional group and its reactivity on surfaces, we synthesized a prochiral precursor molecule presenting an indenofluorene backbone with two CBr₂ groups. Upon sublimation on surfaces the homocoupling reaction took place at room temperature. Three different substrates were employed: Au(111), Ag(111) and Ag(100), to elucidate the chemical role of the metal and of the substrate termination.

On all the surfaces, long polymers were found based on cumulene bridges. On Au(111) the polymers display racemic segments, a result of the random mixture the two molecular enantiomers. However, on Ag(100) and Ag(111), the polymers display more homochiral segments than the ones formed on Au(111) by a factor of 2. We can conclude that, depending on the substrate, it is possible to steer the homochirality of the designed molecular wires. Our results represent a step further towards a better control of the on-surface synthesis of homochiral polymers.

O 103.2 Thu 13:30 P

On-surface synthesis of doubly-linked one-dimensional pentacene ladder polymer — ●KALYAN BISWAS¹, JOSÉ I. URGEL¹, ANA SÁNCHEZ-GRANDE¹, SHAYAN EDALATMANESH², JOSÉ SANTOS¹, BORJA CIRERA¹, PINGO MUTOMBO², KOEN LAUWAET¹, RODOLFO MIRANDA¹, PAVEL JELÍNEK², NAZARIO MARTÍN¹, and DAVID ÉCIJA¹ — ¹IMDEA Nanoscience, 28049 Madrid, Spain — ²Institute of Physics of the Czech Academy of Science, CZ-16253 Prague, Czech Republic

π -conjugated polymers have received great attention in basic and applied research fields as promising new materials for the fabrication of semiconducting devices due to their unique electronic properties. The traditional solution synthesis of such material has been extended to the new synthetic discipline of on-surface synthesis, being based on the reaction of molecular precursors on surfaces in ultra-high vacuum conditions. Here, we provide a synthetic protocol toward the on-surface synthesis of ethynylene-like doubly-connected pentacene polymers by sublimation of pentacene derivatives with =CBr₂ moieties and subsequent annealing on Au(111). The characterization of the polymers was performed by low-temperature scanning tunneling microscopy and non-contact atomic force microscopy, complemented with density functional theory calculations, revealing the formation of an unprecedented ethylene-like bridged pentacene ladder polymer. We envision that our study will be of general relevance for the synthesis and characterization of π -conjugated polymers opening new avenues with prospects for applications in molecular optoelectronics.

O 103.3 Thu 13:30 P

Formation of Polymeric Chains via On-Surface Coupling of Aldehydes — ●NAN CAO¹, MARYAM EBRAHIMI^{1,2}, ALEXANDER RISS¹, EDUARDO CORRAL-RASCON¹, ALEKSANDR BAKLANOV¹, WILLI AUWÄRTER¹, and JOHANNES V. BARTH¹ — ¹Physics Department E20, Technical University of Munich, D-85748 Garching, Germany — ²Department of Chemistry, Lakehead University, P7B 5E1 Thunder Bay, Ontario, Canada

On-surface reactions provide new prospects for the formation of well-defined nanostructures stabilized by covalent bonds. Within the last decade, inspired by classic organic reactions, many pathways were demonstrated on single crystal surfaces under ultrahigh vacuum conditions. Precursors and products can be directly characterized by scanning probe techniques with atomic resolution in real space. Here, we report on a new coupling reaction using aromatic aldehyde species. The deposition of aldehyde precursors on Ag(111), followed by a post-annealing treatment, resulted in the formation of ordered polymeric chains. Scanning tunneling microscopy (STM) provides insights into the structural evolution before and after the coupling reaction. Our non-contact atomic force microscopy and high-resolution STM data

illustrate the linkage of carbonyl groups in the periphery of the reactants. Based on these insights, and taking into account complementary X-ray photoelectron spectroscopy measurements and density functional theory calculations, we develop a coherent picture of the reaction pathway. Our findings introduce a new avenue for the on-surface synthesis of ordered covalent nanostructures.

O 103.4 Thu 13:30 P

Investigating the mechanism underlying an order-disorder transition for molecular assemblies of tetraphenylporphyrin (TPP) on Au(111) — ●MATTHEW EDMONDSON¹, ELEANOR FRAMPTON^{1,2}, CHRIS J. JUDD¹, NEIL R. CHAMPNESS², DAVID A. DUNCAN³, ROBERT JONES², and ALEX SAYWELL¹ — ¹School of Physics & Astronomy, University of Nottingham — ²School of Chemistry, University of Nottingham, Nottingham, UK — ³Diamond Light Source, Harwell Science and Innovation Campus, Didcot, UK

Porphyrins display a rich array of chemical and physical properties which can be tuned by incorporating a metal atom via solution-phase synthesis or on-surface protocols.[1] Self-metalation (uptake of metal atoms from a supporting substrate) has been observed for surface confined porphyrin species, such as for 2H-tetraphenylporphyrin (2H-TPP) on Cu(111),[2] and offers an alternate synthetic pathway for the formation of metalated TPP (M-TPP) which is driven by interaction with the substrate.

Here we report on the interaction between 2H-TPP and Au(111) and present details of an order-disorder transition of 2H-TPP assemblies. Chemical analysis via X-ray photoelectron spectroscopy (XPS) suggests the formation of an Au-TPP species as part of this process. Characterisation using a combination of scanning probe microscopy, XPS, and X-ray standing wave techniques provide both chemical and structural information on the evolution of this on-surface reaction.

[1] J. M. Gottfried, Surface Science Reports, 2015, 70, 259-379.

[2] K. Diller et al., Journal of Chemical Physics, 2012, 136, 14705.

O 103.5 Thu 13:30 P

Interfacial chemical bonding of protective (Ti,Al)N coatings grown on polycarbonate — ●LENA PATTERER, SOHEIL KARIMI AGHDA, DAMIAN MAURITIUS HOLZAPFEL, and JOCHEN MICHAEL SCHNEIDER — Materials Chemistry, RWTH Aachen University, Kopernikusstr. 10, 52074 Aachen, Germany

Due to its superior mechanical properties as well as oxidation resistance, (Ti,Al)N coatings are commonly used as protective coatings for cutting and forming tools. However, less attention has been drawn so far to its application as protective coatings onto polymer components. To identify the chemical reactions and the corresponding bond formation at the (Ti,Al)N | polycarbonate interface, a detailed X-ray photoelectron spectroscopy analysis is performed on pulsed direct current magnetron sputtered (DCMS) (Ti,Al)N coatings deposited onto polycarbonate. To this end, the coating thickness was less than 2 nm to ensure that the chemical state information including the interfacial region is probed. By comparing to the chemical state information of the uncoated polycarbonate, the formation of CN_x as well as of C-O-(Ti,Al) bonds is identified. Hence, it is reasonable to assume that these bonds serve as chemical link across the interface and firmly anchor the (Ti,Al)N coating on the polycarbonate substrate.

O 103.6 Thu 13:30 P

Production of oxidized C₆₀ on carbonaceous substrates — ●GEORGIOS PANTAZIDIS¹, ANDREW CASSIDY¹, JOHN DAVID THROWER¹, and LIV HORNEKAER^{1,2} — ¹Department of Physics and Astronomy, Aarhus University, 8000 Aarhus C, Denmark — ²Interdisciplinary Nanoscience Center (iNANO), Aarhus University, 8000 Aarhus C, Denmark

In this poster, data characterising the production of C₆₀ oxides on a graphitic surface, in conditions that mimic interstellar environments, are presented. Experiments were performed in an ultra-high vacuum chamber with a base pressure of 5 × 10⁻¹⁰ mbar. Thin films of C₆₀ were prepared by *in situ* dosing on a highly oriented pyrolytic graphite (HOPG) substrate. Oxygen atoms were produced *via* thermal cracking through a hot capillary which is heated to *ca.* 1850 K. Surface science techniques like temperature programmed desorption (TPD), scanning tunnelling microscopy (STM) and X-ray photoelectron spectroscopy

(XPS), were used for the experimental investigation. Findings suggest that $C_{60}O_x$ are formed, with oxygen atoms chemisorbing on the C_{60} molecule, forming ether and epoxide functional groups. Upon thermal annealing, the $C_{60}O_x$ fragment into C_yO_z and species like CO and CO_2 , which lead to the formation of thermally stable remnants on top of the HOPG, creating a porous carbonaceous substrate (m-HOPG). When the $C_{60}O_x$ were produced on the m-HOPG substrate, the reactivity towards oxygen atoms was higher and, apart from ether and epoxide groups, carbonyl groups were also present, suggesting a more complex chemistry, aided by the porous substrate.

O 103.7 Thu 13:30 P

Highly selective synthesis of enetriyne via tetramerization of terminal alkynes on Ag(100) — NAN CAO¹, •BIAO YANG¹, JONAS BJÖRK², and JOHANNES V. BARTH¹ — ¹Physics Department E20, Technical University of Munich, D-85748 Garching, Germany — ²Department of Physics, Chemistry and Biology, IFM, Linköping University, 58183 Linköping (Sweden)

Enetriyne, a conjugated species of eneyne family, is a prominent con-

stituent in the antibiotic and antitumor sector. On-surface synthesis under ultrahigh vacuum, which can be monitored by real space scanning probe microscopy and other techniques, has been widely used as a powerful tool to disentangle and control reaction pathways on well-defined interfaces. We herein report a novel approach of enetriyne formation with high selectivity via tetramerization of terminal alkynes on Ag(100). Taking advantage of a hydroxyl directing group, we managed to steer the reaction process and obtain a uniform product. Firstly, upon O₂ exposure the adsorbed precursor's terminal alkyne moieties deprotonate, which entails the formation of organometallic dimer. Secondly, controlled annealing of the pretreated sample induces the formation of the tetrameric species, which self-assembles in regular islands stabilized by lateral weak interactions. We combine STM, XPS studies and DFT calculations to examine the newly formed covalent compounds and suggest a reaction mechanism. Our study provides a protocol, involving a directing group, gas-mediated pretreatment, and an excitation reaction to precisely fabricate a functional enetriyne species.