

## O 55: Organic Molecules on Inorganic Substrates IV: Adsorption and Growth II

Time: Wednesday 15:00–17:45

Location: CHE 91

O 55.1 Wed 15:00 CHE 91

**Bias-dependent conductivity switching and rectification in metallocene-based molecular junctions** — YANGBIAO LIU<sup>1</sup>, ANDIKA ASYUDA<sup>1</sup>, HEINRICH LANG<sup>2</sup>, EGBERT ZOJER<sup>3</sup>, and MICHAEL ZHARNIKOV<sup>1</sup> — <sup>1</sup>Angewandte Physikalische Chemie, Universität Heidelberg, 69120 Heidelberg, Germany — <sup>2</sup>Fakultät für Naturwissenschaften, Anorganische Chemie, Technische Universität Chemnitz, D-09107 Chemnitz, Germany — <sup>3</sup>Institute of Solid State Physics, NAWI Graz, Graz University of Technology, 8010 Graz, Austria

Self-assembled monolayers (SAMs) of ferrocenyl/ruthenocenyl-substituted biphenylthiolates and fluorenylthiolates on Au(111) exhibit two distinct conductance states (CS) in two-terminal junctions featuring a sharp tip of eutectic GaIn as top electrode. When only negatively biasing the junction, the original, high CS is preserved, while the junction is switched to a low CS when applying only positive biases. Comparing the current values for these two states, one gets an effective rectification ratio of more than 1000 - a value comparable to the best performing molecular diodes but attained already at particularly low voltages. Significantly, the switching between the conduction states is reversible and the initial, high CS can be recovered by the application of a negative bias. Moreover, as shown by the example of one of the SAMs studied, when sweeping the junction alternately to the maximum positive and negative bias voltages (as usually done in literature), fully symmetric J-V curves are observed. This means that for a symmetric sweeping of the junction, the effective rectification disappears.

O 55.2 Wed 15:15 CHE 91

**Sensing properties of cerium oxide as an electrode material for the detection of glucose** — ANASTASIIA DEINEKO<sup>1</sup>, VICHESLAV KALINOVYCH<sup>1</sup>, SASCHA L. MEHL<sup>2</sup>, YEVHENIIA LOBKO<sup>1</sup>, YURIY YAKOVLEV<sup>1</sup>, TOMÁŠ SKÁLA<sup>1</sup>, KEVIN C. PRINCE<sup>2</sup>, VLADIMÍR MATOLÍN<sup>1</sup>, IVA MATOLÍNOVÁ<sup>1</sup>, and NATALIYA TSUD<sup>1</sup> — <sup>1</sup>Charles University, Faculty of Mathematics and Physics, Department of Surface and Plasma Science, Prague, Czech Republic — <sup>2</sup>Elettra-Sincrotrone Trieste S.C.p.A., Basovizza, Trieste, Italy

Detection of glucose level in biological liquids is of great importance nowadays because of the growing number of people with diabetes. A variety of oxides is used as electrode material for biosensors and cerium oxide is among them due to its unique properties. In this study characterization of the cerium oxide was performed by surface analysis techniques using photoelectron and absorption spectroscopies (XPS, SRPES, RPES, NEXAFS) in combination with electrochemical measurements. Photoemission based analysis provided information on changes in the oxidation state of cerium cations on the surface and in the subsurface layers of the oxide film, and whether glucose chemically bonds to the oxide. While electrochemical testing, namely cyclic voltammetry and chronoamperometry, was used to explore the sensing properties of polycrystalline cerium oxide films in reaction with glucose in the PBS working solution. The CeO<sub>2</sub> working electrode sensitivity and pH range of sensor stability were determined and discussed in view of the enzymatic properties of cerium oxide. Keywords: cerium oxide, glucose, photoelectron spectroscopy, electrochemistry, biosensor.

O 55.3 Wed 15:30 CHE 91

**Exploiting Cooperative Catalysis for the On-Surface Synthesis of Linear Heteroaromatic Polymers via Selective C-H Activation** — XUNSHAN LIU<sup>1</sup>, ADAM MATEJ<sup>2,3</sup>, TIM KRATKY<sup>4</sup>, JESÚS I. MENDIETA-MORENO<sup>2</sup>, SEBASTIAN GÜNTHER<sup>4</sup>, PINGO MUTOMBO<sup>2</sup>, SILVIO DECURTINS<sup>1</sup>, ULRICH ASCHAUER<sup>1</sup>, JASCHA REPP<sup>5</sup>, PAVEL JELINEK<sup>2,3</sup>, SHI-XIA LIU<sup>1</sup>, and LAERTE L. PATERA<sup>4,5,6</sup> — <sup>1</sup>Department of Chemistry, Biochemistry and Pharmaceutical Sciences, University of Bern, Bern, Switzerland — <sup>2</sup>Institute of Physics of Czech Academy of Sciences, Prague, Czech Republic — <sup>3</sup>Regional Centre of Advanced Technologies and Materials, Palacký University Olomouc, Olomouc, Czech Republic — <sup>4</sup>Department of Chemistry, Technical University of Munich, Garching, Germany — <sup>5</sup>Institute of Experimental and Applied Physics, University of Regensburg, Regensburg, Germany — <sup>6</sup>Institute of Physical Chemistry, University of Innsbruck, Austria

Regiospecific C-H activation is a promising approach to achieve extended polymers. Herein, selective C-H activation for dehydrogenative

C-C couplings of hexaazatriphenylene by Scholl reaction on Ag(111) is reported. By means of low-temperature scanning probe microscopy, we revealed the formation of one-dimensional polymers with a double-chain structure [1]. The growth process is rationalized by density functional theory calculations, pointing out a cooperative catalytic action of Na and Ag adatoms in steering the selective polymerization.

[1] X. Liu, et al., *Angew. Chem. Int. Ed.* 2013 61.5 (2022): e202112798.

O 55.4 Wed 15:45 CHE 91

**PTCDA mediated Ag(111) step reconstruction as precursor to pinwheel phase** — DANYANG LIU<sup>1</sup>, ALEŠ CAHLÍK<sup>1</sup>, CAROLINA A. MARQUES<sup>1</sup>, JENS OPPLIGER<sup>1</sup>, RUSLAN TEMIROV<sup>2,3</sup>, and FABIAN D. NATTERER<sup>1</sup> — <sup>1</sup>Department of Physics, University of Zurich, Winterthurerstrasse 190, CH-8057 Zurich, Switzerland — <sup>2</sup>Peter Grünberg Institut (PGI-3), Forschungszentrum Jülich, 52425 Jülich, Germany — <sup>3</sup>University of Cologne, Faculty of Mathematics and Natural Sciences, Institute of Physics II, 50937 Cologne, Germany

PTCDA (3,4,9,10-Perylenetetracarboxylic dianhydride) forming herringbone islands on Ag(111) is the most striking phase and the prototypical metal-supported organic semiconductor. When we co-deposit PTCDA and Ag on Ag(111) at room temperature, we find that prior to their self-assembly into PTCDA herringbone islands, the molecules implant themselves into and reshape the Ag step edges. The PTCDA-decorated-Ag steps are curved and, depending on whether the Ag steps originate from screw dislocations or a terrace, cause steps reconstruction into multilayer high spirals or isolated Ag islands that both exhibit quantum confinement. At higher coverages, the PTCDA decorated steps may nucleate a distinct pinwheel phase that occasionally proceeds to form a metal-organic framework. Annealing to higher temperatures straightens the PTCDA/Ag steps and may grow more pinwheel phase PTCDA patches, showing yet another tuning knob for organometallic surface science.

O 55.5 Wed 16:00 CHE 91

**Growth of ordered two-dimensional cobalt phthalocyanine films on a one-dimensional substrate** — MILAN KUBICKI, SUSI LINDNER-FRANZ, MARIO DÄHNE, and MARTIN FRANZ — Technische Universität Berlin, Institut für Festkörperphysik, Berlin, Germany

The formation of self-assembled layers of organic materials on solid surfaces is an important subject because of their possible application in advanced (opto-) electronic devices. While such a formation of self-assembled monolayers is well established on metal surfaces, the growth on silicon surfaces is much less studied.

Using scanning tunneling microscopy (STM) the molecular arrangement of cobalt phthalocyanine (CoPc) molecules on the In-Si(111)-(4 × 1) surface is studied [1]. CoPc belongs to the transition metal phthalocyanines being a class of organic semiconductors, which has been already employed e.g. in organic light emitting diodes, in organic photovoltaic cells, and in organic field-effect transistors.

Our data demonstrate that for low CoPc coverages the molecules are highly mobile along the In-Si nanowires. By approaching the saturation coverage, the CoPc molecules stabilize each other by forming a highly ordered two-dimensional monolayer. Based on STM observations a structure model with a (4 × 4) periodicity could be developed, which precisely explains the experimental observations.

[1] M. Kubicki, S. Lindner-Franz, M. Dähne, and M. Franz, *Appl. Phys. Lett.* 119, 133105 (2021).

**Topical Talk**

O 55.6 Wed 16:15 CHE 91

**Towards Understanding and Controlling On-Surface Reactions and Self-Assembly Mechanisms** — DANIEL EBELING — Institute of Applied Physics, Justus Liebig University Giessen, Heinrich-Buff-Ring 16, 35392 Giessen, Germany

The ability to construct organic nanomaterials with atomic precision is the key for applications in molecular electronics as the (opto-)electronic properties of such quantum materials depend on their atomic structure and size. To develop new strategies for synthesizing organic nanomaterials on surfaces, in-depth knowledge about the reaction processes and self-assembly mechanisms is needed. This can be revealed by visualizing the chemical structure and orientation of individual reaction intermediates using bond imaging atomic force microscopy (AFM).

In this presentation, recent results will be discussed that offer an approach for tuning the self-assembly process of halogenated compounds via reversing the binding selectivity of intermolecular halogen bonds. [1] A strategy for building covalent nanostructures one molecule at a time on an inert sodium chloride surface via scanning probe manipulation is also presented. This enables synthesizing elusive covalent nanoarchitectures, studying structural modifications and revealing pathways of intermolecular reactions. [2] Moreover, possibilities for tweaking the bond imaging technique using torsional and flexural higher eigenmodes of qPlus sensors will be illustrated. [3]

[1] J. Tschakert et al. *Nature Communications* 11, 5630 (2020)

[2] Q. Zhong et al. *Nature Chemistry* 13, 1133 (2021)

[3] D. Martin-Jimenez et al. *Nanoscale* 14, 5329 (2022)

O 55.7 Wed 16:45 CHE 91

**Molecular orientation of DHTAP on the nanostructured Cu-CuO stripe phase** — •CLAUDIA LÓPEZ-POSADAS<sup>1</sup>, ANTONY THOMAS<sup>2</sup>, THOMAS LEONI<sup>2</sup>, OLIVIER SIRI<sup>2</sup>, CONRAD BECKER<sup>2</sup>, and PETER ZEPPENFELD<sup>1</sup> — <sup>1</sup>Institute of Experimental Physics, Johannes Kepler University Linz, Altenberger Str. 69, 4040 Linz, Austria — <sup>2</sup>Aix-Marseille University, CNRS, CINaM, UMR 7325, F-13288 Marseille, France

We have studied the preferential adsorption, structure and molecular orientation of 5,14-dihydro-5,7,12,14-tetraazapentacene (DHTAP) layers on the regularly patterned Cu-CuO stripe phase obtained by sub-monolayer oxygen adsorption on the Cu(110) surface. Using Reflectance Difference Spectroscopy (RDS) and Scanning Tunneling Microscopy (STM) we find that the DHTAP molecules preferentially adsorb on the Cu (110) stripes, where they are always lying flat with their long molecular axis aligned parallel to the [-110]-direction. In contrast, on the subsequently covered Cu(110)-(2x1)O stripes, the DHTAP molecules are aligned with their long molecular axis parallel to the [001]-direction. The evolution of the RDS signal allows to monitor the sequential adsorption and orientation of DHTAP during monolayer formation and the subsequent multilayer growth for different oxygen pre-coverages and, hence, different Cu and CuO stripe widths. Interestingly, beyond the first monolayer, the DHTAP molecules adopt a preferential orientation which critically depends on the initial oxygen coverage, revealing the influence of the Cu-CuO stripe width and the possibility to tune the overall optical anisotropy of these films.

O 55.8 Wed 17:00 CHE 91

**Oxygen-induced reorientation of organometallic chains on Cu(110)** — •ILIAS GAZIZULLIN, CHRISTOPHE NACCI, and LEONHARD GRILL — Physical Chemistry Department, University of Graz, Heinrichstraße 28, Graz, Austria

The deposition of molecules onto crystalline surfaces allows their investigation at the single-molecule level by scanning tunneling microscopy (STM). It furthermore gives access to the controllable on-surface synthesis of covalent polymers [1]. Here, we have studied dibromo-*p*-terphenyl molecules on Cu(110) and on the Cu(110)-(2x1)O striped phase under ultra-high vacuum conditions with low-temperature STM.

Previously, the Cu(110)-(2x1)O striped phase was used as a template for the synthesis of organometallic structures having different sizes and shapes depending on the width of copper stripes [2]. The focus of our study is how pre- or post-adsorbed oxygen and annealing, which is necessary for covalent polymerization, affect the molecular adsorption on the surface. It turns out that on the striped phase the molecules form organometallic chains on the copper areas, oriented in at least three surface directions. Increasing the sample temperature from 300

K to 450 K induces a reorientation of the organometallic chains, which occurs due to stabilization of the reoriented OM chains by embedding in the Cu-O phase.

References

[1] L. Grill, S. Hecht, *Nature Chemistry* 12, 115-130 (2020)

[2] Q. Fan, J. Dai, T. Wang, J. Kuttner, G. Hilt, J. M. Gottfried, and J. Zhu, *ACS Nano* 3, 3747 (2016)

O 55.9 Wed 17:15 CHE 91

**Simulations of 1D Supramolecular Chains on Gold with Explicit Surface-Substrate Interactions** — •KRYSTOF BREZINA<sup>1,2</sup>, HUBERT BECK<sup>1</sup>, MARIANA ROSSI<sup>2</sup>, and ONDREJ MARSALEK<sup>1</sup> — <sup>1</sup>Charles University, Faculty of Mathematics and Physics, Prague, Czech Republic — <sup>2</sup>Max-Planck-Institut für Struktur und Dynamik der Materie, Hamburg, Germany

2,5-diaminobenzoquinone-1,4-diimine molecules deposited on Au(111) have been observed in AFM experiments to assemble into 1D hydrogen-bonded chains, which exhibit different geometries and mechanical properties depending on the conditions at the deposition [1]. While a complete explanation of this behavior remains elusive, it is clear that nuclear quantum effects on the hydrogen bonding play an important role. To clarify this effect, we aim at performing path integral molecular dynamics with *ab initio*-quality potentials, in a system that explicitly takes into account molecules and the surface. Here, we discuss the methodological advances needed to generate meaningful training sets for the neural network potentials that substitute the reference *ab initio* method, in particular when a reaction needs to be well described [2]. We show the nature of the relevant proton-transfer *ab initio* potential energy surfaces as well as initial results focusing on the specific effects of the surface on the geometry of the molecules and on the character of the nuclear quantum effects in the chains.

[1] Cahlik A. et al. *ACS Nano* 2021, 15, 6, 10357-10365

[2] Brezina K., Beck H. and Marsalek O. *In preparation* 2022

O 55.10 Wed 17:30 CHE 91

**Controlled Formation of Porous 2D Lattices from C<sub>3</sub> Symmetric Ph<sub>6</sub>-Me-Tribenzotriquinacene-OAc<sub>3</sub>** — •MARKUS LEISEGANG<sup>1</sup>, SINEM TOKSABAY<sup>1</sup>, ANDREAS CHRIST<sup>1</sup>, PATRICK HÄRTL<sup>1</sup>, JOHANNES KREBS<sup>1</sup>, TODD B. MARDER<sup>1</sup>, SOUMYAJYOTI HALDAR<sup>2</sup>, STEFAN HEINZE<sup>2</sup>, MATTHIAS BODE<sup>1</sup>, and ANKE KRUEGER<sup>1,3</sup> — <sup>1</sup>Universität Würzburg, Germany — <sup>2</sup>Universität Kiel, Germany — <sup>3</sup>Universität Stuttgart, Germany

The on-surface self-assembly of molecules is a promising approach to control the properties of resulting 2D lattices. Usually, planar molecules are utilized to prepare flat, structurally confined molecular layers, with only a few recent examples of warped precursors [1,2]. However, detailed control of the superstructures is limited thus far. Herein, we report the temperature-controlled self-assembly of a bowl-shaped, acetylated C<sub>3</sub>-symmetric hexaphenyl-tribenzotriquinacene derivative on Cu(111). Combining scanning tunneling microscopy (STM) and density functional theory (DFT) confirms the formation of highly differing arrangements starting with  $\pi$ -stacked bowl-to-bowl dimers at low coverage at room temperature via chiral honeycomb structures, an intermediate trigonal superstructure, followed by a fully carbon-based, flattened hexagonal superstructure formed by on-surface deacetylation, which is proposed as a precursor for holey graphene networks with unique defect structures [3].

[1] T. Lohr et al., *J. Am. Chem. Soc.* 142, 13565 (2020)

[2] J. Urgel et al., *J. Am. Chem. Soc.* 141, 13158 (2019)

[3] S. Toksabay et al., *Chem. Eur. J.* 2022, e202203187 (2022)