O 6: Organic Molecules on Inorganic Substrates I: Adsorption & Growth

Time: Monday 10:30–13:00 Location: MA 042

O 6.1 Mon 10:30 MA 042

Unraveling Glycan Structures: ESIBD+STM Exploration of Stapled Conformations — •Dhaneesh Kumar[1], Kelvin Anggara[1], Manuel G. Ricardo[2], Peter H. Seeberger[2], and Klaus Kern[1,3] — [1]Max-Planck-Institute for Solid State Research, Stuttgart, Germany — [2]Max-Planck-Institute of Colloids and Interfaces, Potsdam, Germany — [3]École Polytechnique Fédérale de Lausanne, Switzerland

”Function follows form” holds a particular significance in the realm of biomolecules, where structural modifications can profoundly influence functionality. Recently, introduction of linkages or ’staples’ at specific sites within a linear oligosaccharide (a.k.a. glycan) has been demonstrated to alter the biochemical properties of the glycan (1). Despite these advancements, the structural effect of these staples on glycan conformation has yet to be probed directly, leaving the bioactive conformations unknown.

Using Electrospray Ion Beam Deposition (ESIBD), we successfully transferred these stapled glycans onto a surface in vacuum, which are subsequently imaged individually by Scanning Tunnelling Microscopy (STM). By systematically varying factors such as stapling length and sites, we can visualize the possible conformational states of these stapled glycans. This integrated ESIBD+STM approach provides a complementary tool for studying biomolecular conformational states at the single-molecule level, overcoming limitations of conventional techniques.

(1) Ricardo M. G., et al.,J. A. Chem. Soc. (2022)

O 6.2 Mon 10:45 MA 042

Unlocking non-volatile molecular building blocks for atomically clean vacuum depositions — •Andreas Walz[1,2], Annette Huettig[1,2], Michael Walz[1,2], Hartmut Schlichting[1,2], and Johannes V. Barth[1] — [1]Technical University of Munich, Physics E20, Garching, Germany — [2]pureions GmbH, Gilching, Germany

Novel nanostructures of organic and anorganic compounds require precise growth of clean films on well-defined surfaces. Their fabrication is technically limited: Thermal evaporation in vacuum (MBE, OMBE) is constrained to volatile species. Wet/ solution-based techniques (drop casting, spin coating, inkjet printing) are broadly applicable, but often lack purity and quality.

Controlled Ion Beam Deposition (CIBD), realized in a NanoPrinter device from pureions, combines the best of both: a broad range of fragile species under ultra-clean conditions enabled by Electrospray Ionization (ESI) e.g., functionalized small molecules (e.g. linkers for MOFs), graphene nanoribbons, up to large biomolecules like proteins or DNA. Other ion sources such as MALDI, laser vaporization or magnetron sputtering cluster sources are also considered. Transfer of the ions to ultra-high vacuum (UHV) and mass filtering via a digital quadrupole mass filter (dQMF) removes all unwanted neutral or ionic impurities. Soft-landing or if wished, reactive-landing for on-surface chemistry, is both ensured by control of energy and dose. CIBD is a new tool providing functional nanostructures for all kinds of applications, e.g. in organic electronics / photovoltaics / LEDs / sensors / transistors, nanocatalysis, energy storage, molecular packaging, biotech, pharma.

O 6.3 Mon 11:00 MA 042

Growth of ordered cobalt phthalocyanine monolayers on a terbium modified silicon surface — •Milan Kubicki, Martin Franz, and Mario Dähne — Technische Universität Berlin, Institut für Festkörperphysik, Berlin, Germany

The formation of self-assembled layers of organic molecules on solid surfaces is an important subject because of their possible application in advanced optical and electronic devices. While the formation of self-assembled layers is well established on metal surfaces, the growth on silicon surfaces is much less studied.

On pure silicon surfaces the number of dangling bonds leads to a highly reactive surface and often to rather disordered organic films. The modification of silicon surfaces with thin atomic layers is an interesting alternative. Here, a metallic rare earth silicide monolayer is used as a substrate for the molecular growth.

Using scanning tunneling microscopy and spectroscopy the molecular arrangement and the electronic properties of cobalt phthalocyanine (CoPc) molecules on the TbSi$_2$/Si(111) surface are studied. 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, photovoltaic cells, and field-effect transistors.

Our data demonstrate that single CoPc molecules stay mobile at the TbSi$_2$/Si(111) surface at room temperature. By reaching a coverage of a full monolayer a highly ordered film of flat-lying CoPc molecules in different orientations is formed, demonstrating the great potential of rare earth silicides on Si(111) as template for organic film growth.

O 6.4 Mon 11:15 MA 042

Identifying the Surface Arrangement of a Mixed Zinc Tetraphenylporhyrin and Monocarboxyphenyl Triphenylporphyrin Layer on Rutile TiO2(110) Using XPS — •Maximilian Muth, Alexander Wolfram, Hans-Peter Steinrück, and Ole Lytken — Friedrich-Alexander-Universität Erlangen-Nürnberg, Germany

Gaining deeper knowledge about the adsorption behavior of organic molecules on substrate surfaces is crucial for possible applications. One approach to learn about the (relative) adsorption strength of different molecules is to subsequently adsorb different molecules on top of each other at low temperature, and study the preferential displacement of the weaker bound species from the surface upon heating. Using this method, we have identified the relative adsorptions strengths of three tetraphenylporphyrins (ZnTPP, CoTPP, MgTPP) on rutile TiO2(110).[1] Moreover, we have recently addressed layers of these non-functionalized molecules and the carboxylic-acid-functionalized tetraphenylporphyrin (2HMCTPP), which is expected to bind more strongly to the surface. Interestingly, instead of completely displacing the non-functionalized molecules, we found 2HMCTPP to adsorb upright standing on free adsorption sites in between the flat-lying non-functionalized molecules.

[1] Muth et al., Accurate Determination of Adsorption-Energy Differences of Metalloporphyrins on Rutile TiO2(110) 1x1, Langmuir 2022, 38, 28, 8643-8650

O 6.5 Mon 11:30 MA 042

On-surface synthesis of well-aligned pentacene arrays and graphdiyne nanowires on 1D-patterned VSe2 — •Zhongliu Liu[1], Ignacio Piquero-Zulaica[1], Harald Brune[2], and Johannes Barth[1] — [1]Physics Department E20, Technical University of Munich, Germany — [2]Institute of Physics, EPF Lausanne, Switzerland

On-surface synthesis of one-dimensional (1D) polymers is a promising method for creating well-ordered nanostructures, such as graphene nanoribbons and graphdiyne nanowires. Vanadium diselenide (VSe2), as a versatile member from the transition-metal-dichalcogenide family, not only exhibits unique characteristics like ferromagnetism and excellent electrocatalysis, but also presents a unique 1D-patterned structure upon annealing. The pertaining 1D patterns of Se-deficient furrows could influence the positioning of adsorbed molecules and modify their electronic structure, guiding the on-surface synthesis of new organic entities. Here, we present the formation of oriented arrays of pentacene and diethynyl-terphenyl (DETP) 1D polymers on 1D-patterned VSe2. Pentacene arraying along the substrate pattern exhibits a reduced bandgap of approximately 1.60 eV. And for DETP arrangements on the 1D pattern, upon annealing, homocoupling reactions of terminal alkyne tectons entail the formation of oriented nanowires, some of which extend up to 30 molecular units in length. The resulting graphdiyne nanowires show a small energy shift in their HOMO. These findings highlight 1D-patterned VSe2 as a template for modulating the structural and electronic properties of organic molecules, providing a new approach for on-surface synthesis of organic polymers.

O 6.6 Mon 11:45 MA 042

Selectivity in photo- and thermal-induced trans-cis isomerization in the ultra-thin film of azobenzene derivatives on graphite — •Hariom Birla[1], Showkat H Mir[2], Thomas Halbritter[3], Alexander Heckel[4], Jayant K. Singh[5], and Thiruvancheril G. Gopakumar[6] — [1]Department of Chemistry, Indian Institute of Technology Kanpur, Kanpur, UP-208016, India — [2]Department of Chemical Engineering, Indian Institute of Technology Kanpur, Kanpur, UP-208016, India — [3]Eurofins Genomics Germany GmbH, Anzinger Str. 7a, 85560, Ebersberg, Germany — [4]Institute for Organic Chemistry and Chemical Biology, Goethe-University Frankfurt, Max-von-Laue-Str.9, 60438 Frankfurt, Germany — [5]Department of Chemical Engineering, Indian Institute of Technology Kanpur, Kanpur, UP-208016, India — [6]Department of Chemistry, Indian Institute of Technology Kanpur, Kanpur, UP-208016, India

Azobenzene (AB) and its derivatives are known for isomerization between its geometrical isomers using light, temperature, electrons/holes, and electrical field on surfaces. The derivatives of AB could be used as an electronic switch as there is a significant change in the electronic properties upon isomerization (trans-cis). In this work, we show the trans-cis isomerization in the ultra-thin films of azobenzene derivatives on a highly oriented pyrolytic graphite (HOPG)-air interface. The microscopic structure and the on-surface isomerization are investigated using atomic force microscopy (AFM). The trans-to-cis isomerization is induced by a photon of wavelength 360 nm whereas the cis-to-trans isomerization is induced by thermal excitation.

O 6.7 Mon 12:00 MA 042

Density functional theory investigation of Porphine adsorption on the BC monolayer — •Pinar Kaya[1], Çağil Kaderoğlu[1], Ethem Aktürk[2], and Handan Arkin[1] — [1]Department of Physics Engineering, Faculty of Engineering, Ankara University, 06100 Ankara, Turkey — [2]Department of Physics, Adnan Menderes University, 09100, Aydin, Turkey

In recent years, developments in technology have increased the importance of multifunctional, nano-sized, cheap and accessible materials. The first and foremost of these materials is the 2-dimensional (2D) graphene structure [1]. The unique physical, chemical and mechanical properties of 2D graphene have led researchers to investigate new surfaces [2]. In this context, numerous boron-doped graphene (BC_x) structures, whether uniform or non-uniform, have been examined experimentally and theoretically in the literatüre [3,4]. There are very few studies in the literature on BC monolayer, which has not yet been synthesized. In this aim, our study presents first-principle density functional theory calculations for the structural, electronic and magnetic properties of Porphine molecule on the bare doped BC monolayer surface. It is thought that the new functional structures created as a result of the findings will pioneer different application areas. [1] Novoselov, K. S., Geim, A. K., Morozov, S. V., ... & Firsov, A. A. (2004), 306(5696), 666-669. [2] Zhang, H. (2018), 118(13), 6089-6090. [3] Durajski, A. P., & Kasprzak, G. T. (2023), Physica B: Condensed Matter, 660, 414902. [4] Bute, A., Jena, S., Kedia, S., Udupa, D. V., ... & Sinha, S. (2021), Materials Chemistry and Physics, 258, 123860.

O 6.8 Mon 12:15 MA 042

Combining experimentally-measured and DFT-predicted XPS spectra to identify the bond of phenylphosphonic acid to rutile TiO2(110) — •Alexander Wolfram[1], Maximilian Muth[1], Julia Köbl[1], Sascha Mehl[2], Nataliya Tsud[3], Hans-Peter Steinrück[1], Bernd Meyer[1], and Ole Lytken[1] — [1]Uni Erlangen, Germany — [2]Elettra, Italy — [3]Charles Uni, Czech Republic

Anchoring groups, such as carboxylic or phosphonic acids, are common tools to immobilize organic molecules on oxide surfaces and understanding these interfaces is crucial for the optimization of devices like dye-sensitized solar cells. Because the bond to the surface occurs through the oxygen atoms, the O 1s core level region in XPS contains important information about the nature of the bond. However, it is extremely challenging to disentangle the O 1s contribution of the adsorbate from that of the oxide support, as the contribution of the support can significantly change upon adsorption of molecules. We will show how DFT calculations of phenylphosphonic acid on rutile TiO2(110) can be used to predict the full experimentally-measured XPS spectra, based on calculated O 1s binding energies of the oxygen atoms of the adsorbed phenylphosphonic acid molecules as well as the oxygen atoms within the first three trilayers of the surface. The calculated spectra accurately account for both the O 1s contributions of the adsorbed molecules, as well as the change to the O 1s contribution of the rutile TiO2(110) substrate upon adsorption of the molecules.

O 6.9 Mon 12:30 MA 042

"Organic" ab initio thermodynamics for interfaces: Which corners can we (not) cut? — •Christoph Wachter and Oliver T. Hofmann — Institute of Solid State Physics, Graz University of Technology, Graz, 8010, Austria

Ab initio thermodynamics is a powerful tool to computationally predict the most stable structure under given environmental conditions, i.e. at finite temperature and pressure. In principle, this requires evaluating the free energy for a large number of structures, which is a costly endeavor. To keep the computational cost tractable, the current paradigm is to approximate the free energy and neglect several expensive terms, such as the vibrational zero-point energy, the thermal occupation of vibrations and the configuration entropy.

However, these approximations have been developed with simple inorganic adsorbates in mind. It is a priori unclear whether they also hold true for organic/inorganic interfaces, which feature a rich chemistry. Moreover, several effects can occur in these systems (such as cis-trans isomery) that are hardly present for inorganic adsorbates. In this work, we therefore re-evaluate the most common approximations for three conceptually very different systems: a clearly physisorbed system, a covalently bonded self-assembled monolayer, and an interfaces that undergoes charge-transfer reactions. In an attempt to generalize across the different types of interfaces, we discuss which calculations can generally be skipped in order to allow efficient evaluations of the relative stabilities of different phases.

O 6.10 Mon 12:45 MA 042

Understanding the role of adsorbed CTAB in anisotropic nanostructure growth — •Esmée Berger[1], Narjes Khosravian[1], Joakim Löfgren[2], and Paul Erhart[1] — [1]Department of Physics, Chalmers University of Technology, Gothenburg, Sweden — [2]Department of Applied Physics, Aalto University, Espoo, Finland

Surfactants have immense technological relevance. Cetyltrimethylammonium bromide (CTAB) is, for example, commonly used for structural tuning and increased stability during wet-chemical synthesis of nanostructures. The functionality of surfactants is dictated by their phase diagrams, which are often very complex in aqueous solution. The complexity of these systems is further increased during nanostructure growth, due to the presence of surfaces. To improve control over the shapes and sizes of wet-chemically synthesized nanostructures, we must understand the functionality, and thus the structure, of the adsorbed surfactants as these fundamentally alter the nature of the interface, affecting the growth. Phase diagrams are, however, very difficult to probe. To get some insight into the role of surfactants during nanostructure growth we consider CTAB, whose micellar phase has been pointed out as the primary mechanism for anisotropic growth of inorganic nanoparticles. Those results were, however, based on single values of CTAB surface density. To elucidate the role of CTAB in this context, a surface phase diagram must be established. In this work, we use atomistic simulations to develop an understanding of this surface phase diagram from a modeling perspective.