Symposium “Exploring New Horizons with Molecules on Surfaces

16 – 17 Dec. 2024
TUM Institute for Advanced Study (IAS) Lichtenbergstr. 2a, Garching Forschungszentrum

Program

Monday, 16.12.2024

12.00 h	*Snacks, IAS ground floor*
13.00 h	Lifeng Chi, FUNSOM, Soochow University *On-Surface Hydrocarbon Chemistry*
13.50 h	Xinliang Feng, MPI of Microstructure Physics & TU Dresden *Graphene Nanostructures 3.0: Quantum Phenomena & Properties*
14.40 h	Pavel Jelinek, Institute of Physics of the CAS, Prague *Theoretical insight into the course of on-surface chemical reactions*
15.30 h	*Coffee break*
16.00 h	Daniel Ebeling, Justus Liebig University Giessen *Constructing organic nanomaterials molecule by molecule and deciphering on-surface reaction processes via chemical bond imaging*
16.50 h	Mathias Senge, Trinity College Dublin, The University of Dublin *Into the Frying Pan – Cool Molecules on Hot Surfaces*
17.40 h	Ana Sanchez, Institute of Physics of the CAS, Prague *On-surface synthesis of a large-scale 2D MOF with competing π-d ferromagnetic/antiferromagnetic order*
18.10 h	Contributed talks – Session I
19.15 h	*Dinner at Faculty Club*

Tuesday, 17.12.2024

09.30 h	Johanna Eichhorn, NAT School *Understanding nanoscale working interfaces for energy conversion*
10.10 h	Willi Auwärter, NAT School *On-Surface Synthesis of O-substituted Porphyrins and BN-Substituted Carbon Networks*
10.50 h	Kelvin Anggara, MPI for Solid State Research, Stuttgart *Analyzing structures of biomolecules at the single molecule level by direct imaging on surface*
11.40 h	Andreas Walz, pureions GmbH, NAT School
12.10 h	*Lunch buffet at Faculty Club*
13.30 h	Sebastian Günther, NAT School *On the thermodynamics and kinetics of graphene growth on Cu and the properties of the synthesized material*
14.10 h	Markus Lackinger, Deutsches Museum *Synthesis on Less Reactive to Inert Surfaces*
14.50 h	Contributed talks – Session II
ca. 16.30 h	*Coffee and End of Symposium*

Invited / Keynote Speakers:

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Auditorium (ground floor) and Faculty Club (4th floor)

On-Surface Hydrocarbon Chemistry

Lifeng Chi

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On-surface chemistry is an emerging interdisciplinary discipline developed in recent years, which presents the great potential in breaking through limitations of traditional chemical synthesis and accurately preparing functional molecular nanostructures. We have made a series of explorations to address the challenging scientific problem of selective C-H bond activation and C-C coupling of saturated alkanes on Au(110) surface [1,2], and further realizing the conversion of alkanes to conjugated polyenes on the surface of Cu(110) as well as interpreting the underline mechanisms[3-8]. More recently, we demonstrated the high selective dehydrogenative aromatization of n-alkane on different metal surfaces[9]. Thereby new methods for the on-surface conversion from n-alkane to conjugated polyene and their aromatization are established.

[1] D. Y. Zhong et al., *Science*, 334, 213 (2011)

[2] K.W. Sun et al., *J. Am. Chem. Soc.* 140. 4820 (2018)

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[5] Z.M. Hao et al., *J. Phys. Chem. Lett. 13, 3276* (2022)

[6]Y.N.Tang et. al., *Angew. Chem. Int. Ed*, 61, e202204123 (2022)

[7]L.N.Wang et al., *Angew. Chem. Int. Ed*, (2024) online

[8]S.F. You et al., Nat. Commun. (2024) online

[9]L.N.Wang et al., *Angew. Chem. Int. Ed*, (2024) accepted

Graphene Nanostructures 3.0: Quantum Phenomena & Properties

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With the advances in emergent quantum technologies, such as quantum computing, quantum communications, etc., graphene nanostructures provide a unique molecular toolbox for accessing their unprecedented quantum phenomena and topological properties. In this lecture, we will introduce our recent efforts towards the precision graphene nanostructures as the defined quantum entities for the spin-spin coupling. Both in-solution and on-surface synthesis approaches will be discussed that provide synthetic access to this class of unique graphene nanostructures with controlled spin-orbital coupling behavior. We will delve into the synthesis and characterization of individual open-shell graphene molecules, including Kekuléne, non-Kekuléne, and concealed non-Kekuléne structure motifs. Our focus has been on developing these molecular materials with controlled quantum states—singlet, triplet, and high-spin states—to harness their potential as quantum bits (qubits) in quantum computing. Next, we will discuss the collective carbon magnetism and spin coupling in the dimers or trimers of open-shell graphene molecules. As the next step, spin-chains with fractional edge excitations will also be presented. We will explore how interactions between multiple graphene units can lead to complex magnetic phenomena, which are crucial for understanding and developing new forms of quantum materials. Finally, the vision towards the spin-lattice or 2D spin-array will be provided.

Theoretical insight into the course of on-surface chemical reactions

Pavel Jelínek[1]

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On-surface synthesis in ultra-high vacuum conditions has demonstrated the capability to synthesize molecular structures that are not available through traditional methods in solutions.

But what makes the on-surface synthesis on metallic surfaces unique concerning synthesis in solution besides the 2D constraint imposed by the proximity of the surface? Recently, the essential catalytic role of single atoms diffusing on metal surfaces [1], so-called adatoms, at elevated temperatures has been pointed out [2].

To get more insight into the role of adatoms, we employed theoretical simulations employing the free energy QM/MM method to get more insight into the reaction course. The simulations show that single adatoms not only substantially lower the activation barrier for cleavage of strong covalent bonds such as C-H, C-C or C-X, but they also energetically stabilize the resulting intermediate passivating the carbon radical left after breaking the covalent bond.

We will discuss several examples demonstrating the importance of single metal adatoms in on-surface reaction mechanisms. Namely, we will show that decoupling metal adatoms from their native surface can significantly enhance their catalytical activity. Namely, we will discuss that single gold adatom deposited on Ag(111) surface induces highly regioselective cleavage of the C-H bond on aromatic anthracene complexes at room temperature [3]. In addition, we will demonstrate that single Au adatoms are responsible for unusual skeleton rearrangement of hydrocarbons [4] as well as the formation of radical long-range supramolecular networks on metallic surfaces. [5].

Finally, we will also disucss the stability of radicals on metal surfaces and their role in the on-surface reactions.

References

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[2] Zh. Zhang et al, *JPCL* 12, 11061 (2021); J.I. Mendieta-Moreno et al, *Angew. Chem. Int. Ed.* 61 e202208010 (2022); J. Bjork et al, *Angew. Chem. Int. Ed.* 61, e2022123 (2022); K. Biwas et al., Angew. Chem. Int. Ed. 63 e202318185 (2024); E. Perez-Elvira et al, *Nature Synthesis* 2 (12), 1159-1170 (2023).
[3] B. Lowe et al, JACS 144, 21389 (2022).
[4] J.I. Mendieta-Moreno et al, *Angew. Chem. Int. Ed.* 61 e202208010 (2022)
[5] F. Frezza, et al, *J. Am. Chem. Soc.* 146, 3531 (2024)

Constructing organic nanomaterials molecule by molecule and deciphering on-surface reaction processes via chemical bond imaging

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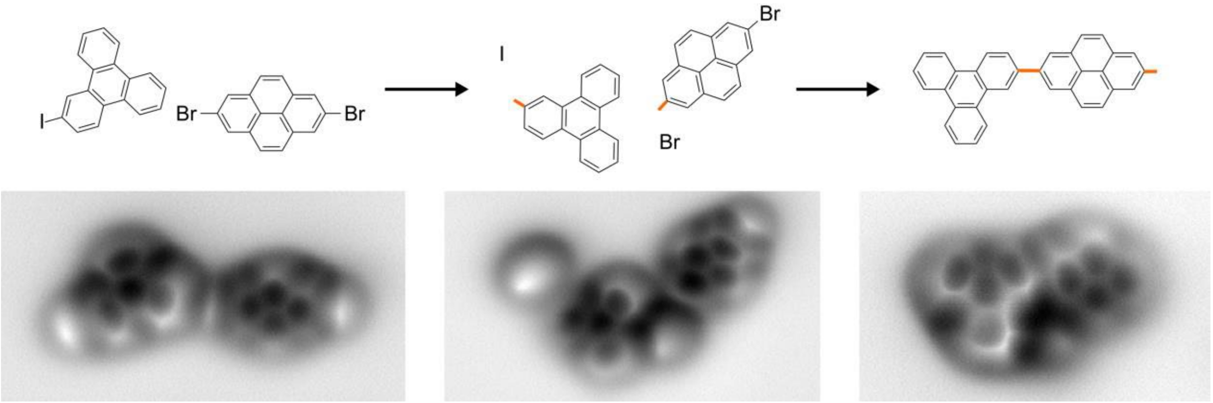
Constructing low-dimensional covalent assemblies with tailored size and connectivity is the key for applications in molecular electronics where optical and electronic properties of the quantum materials are highly structure dependent. We present a versatile approach for building such structures molecule by molecule on bilayer sodium chloride (NaCl) films with the tip of an atomic force microscope, while tracking the structural changes with single-bond resolution. [1] Covalent homo-dimers in *cis* and *trans* configurations and homo-/hetero-trimers were selectively synthesized by a sequence of dehalogenation, translational manipulation and intermolecular coupling of halogenated precursors (see Figure). Using scanning probe manipulation, we were also able to synthesize the structurally elusive molecule P_3N_3, an inorganic aromatic benzene analogue, which is difficult to obtain via traditional synthetic methods due to its high reactivity. [2] This work shows ways for synthesizing elusive molecules and organic nanoarchitectures, studying structural modifications and revealing pathways of intermolecular reactions. Moreover, possibilities for tweaking the bond imaging technique using torsional higher eigenmodes of qPlus sensors and an adaptive tip-sample feedback will be illustrated. [3,4] While torsional eigenmodes can be utilized to perform lateral force microscopy with single bond resolution an adaptive feedback mechanism is useful for imaging the molecules and the surface with atomic resolution in a single scan which allows precise determination of adsorption positions.



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[3] D. Martin-Jimenez et al. *Nanoscale* **14**, 5329 (2022)
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Into the Frying Pan – Cool Molecules on Hot Surfaces

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Synthetic organic chemists like unusual molecules. They should be complex or deceptively simple, difficult to make, have peculiar chemical behavior, and an appealing structure. Developing syntheses for complex molecules is considered an ‘art’ and in the lab entails the whole gamut of thermal, photochemical, radical methods employing solution, flow, and solid-state techniques. Therein, reactions between chemical entities occur when the reaction partners meet in a 3D space. Indeed, chemists pride themselves on being able to manipulate intricate three-dimensional intermolecular interactions to achieve stereoselective syntheses.

Controlling the 3D reaction space through confinement is a standard feature in nature (e.g., active sites in enzymes). In chemistry, supramolecular approaches and nanoreactors function along similar lines. Pioneered by physicists, on-surface chemistry offers an intriguing approach to achieve target selection via 1D or 2D confinement control. Initially limited to simple radical-type couplings, the field is now breaking new ground through single atom editing, observation of alternative (stereo)selectivities and novel mechanistic pathways for known reactions, and identification of unprecedented organometallic entities. Yet, it also still is a bit of an ‘art’ reminiscent of the trial-and-error beginnings of organic chemistry in the 19th century. But the current transitioning to the interfacial preparation of functional systems already involves the use of tectons with multiple reaction sites of different reactivity, traceless linkers, sequential reactions, and sets the stage for ‘total synthesis’ approaches akin to those used by synthetic chemists.

Many of the pioneering studies were achieved with simple aromatic compounds such as porphyrins and mostly involved sp/sp^2-coupling reactions. The use and coupling of tectons with sp^3-centers is more difficult due to lower reactivity and higher degrees of conformational flexibility. Yet, cool isosteric aliphatic compounds such as cubane, propellane, or bicyclo[1.1.1]pentane offer spatial (regioselective) definition of reaction sites similar to aromatics, have a distinct analytical footprint in STM/AFM analysis, and possess unique electronic properties (e.g., as isolators or resistors) for use in molecular organic electronics.

On-surface synthesis of a large-scale 2D MOF with competing π-d ferromagnetic/antiferromagnetic order

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Metalorganic frameworks (MOFs) represent an interesting class of versatile materials with important properties, including magnetism. However, the synthesis of atomically precise large-scale 2D MOFs with non-trivial strong magnetic coupling represents a current research challenge. In this work, we present a two-step approach to synthesize large-scale 2D MOFs with strong magnetic coupling with competing ferromagnetic/antiferromagnetic interactions. The synthetic approach consists of the initial formation of an extended supramolecular organic framework on a Au(111) surface, establishing the large-scale order of organic ligands and its subsequent metalation by single atoms assisted by annealing. Moreover, we show that the usage of radical asymmetric organic ligands enables us to form magnetic 2D MOF with strong π-d electron interactions, which shows complex spin interactions beyond the traditional superexchange mechanism. The structural, electronic and magnetic characterization of the 2D MOF was performed by scanning tunneling microscopy/spectroscopy (STM/STS) and non-contact atomic force microscopy, combined by *ab initio* theoretical simulations beyond DFT.

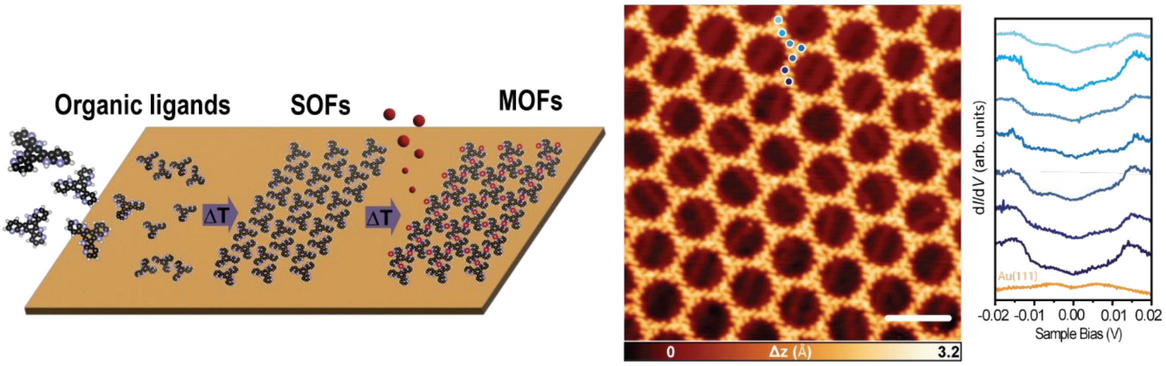

Figure 1:Schematic representation of the two-step synthetic method to grow high-quality 2D MOFs and experimental STM and STS data of the 2D MOF on Au(111).

Understanding nanoscale working interfaces for energy conversion

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Real-world energy materials are subject to nanoscale heterogeneities that control critical structure-function relationships. For example, thin film electrodes are typically polycrystalline exhibiting boundaries between differently orientated grains, different crystal facet orientations, as well as locally varying compositions or phases. Very often, these nano- to micrometer properties impact properties of the macroscale system, such as overall efficiency and stability.

I will discuss our efforts to resolve local structural, chemical, and optoelectronic heterogeneities of different energy materials to understand the impact of their nanoscale properties on macroscopic performance. A particular focus will be to combine insights from different nanoscale techniques to generate a comprehensive picture of charge transport and transfer properties. The gained understanding can be applied to design durable and efficient energy conversion systems.

On-Surface Synthesis of O-substituted Porphyrins and BN-Substituted Carbon Networks

Willi Auwärter, NAT School

On-surface synthesis protocols provide elegant routes to individual molecular complexes, oligomers, and other nanocarbon materials on metal supports [1]. The resulting structural, physical, and chemical properties can be controlled by heteroatom-substitution.

I will present an overview of our activities employing temperature-induced reactions on coinage metal supports in an ultrahigh vacuum environment, affording specific heteroatom-doped porphyrins and BN-substituted nanocarbon materials. Specifically, a route to peripherally O-substituted porphyrins is addressed [2]. Furthermore, tailored BN-doped molecular precursors [3] will be discussed, yielding BN-substituted covalent carbon networks. These include random sheet-like BNC structures [4] that can be transferred to a Si wave dice and covalent organic frameworks (COF) on Ag(111) and Au(111). The characterization by scanning probe microscopy shows that COFs with distinct B_3N_3 densities and pore sizes can be achieved, complementing other BN-doped carbon networks and opening perspectives for further functionalization of BN-patterned surfaces.

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Analyzing structures of biomolecules at the single molecule level by direct imaging on surface

Kelvin Anggara

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Diverse structures of biomolecules in living systems pose challenges for present analytical methods in analyzing their individual molecular structures. Ensemble-averaged measurement on molecules with extensive structural variation leads to loss of structural information for individual molecules.

We herein bypass this problem by imaging and analyzing single biomolecules deposited intact on surfaces. Biomolecules were transferred to the gas-phase by electrospray, mass-selected, and soft-landed at a cold single-crystal metal surface, using the Electrospray Ion Beam Deposition (ESIBD) technique. The deposited molecules were subsequently imaged one-at-a-time by Scanning Tunneling Microscopy (STM) and interpreted by DFT calculations to reveal their individual structures on surface.

We successfully applied our approach to glycans as well as lipids and proteins densely decorated with glycans, whose analyses remain intractable by current analytical methods. Critical to our success is the choice of surfaces to deactivate diffusion and dissociation of biomolecules on surface, as well as the systematic molecular manipulation by the STM tip to unfold the intact biomolecule on surface. The ESIBD+STM+DFT approach opens a new avenue to access individual structures of any biomolecules that can be electrosprayed and deposited onto a surface.

ES-CIBD - enabling UHV deposition of large, reactive or fragile building blocks for functional nano-architectures

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Cutting-edge research in the field surface- and nano-science using organic molecules requires control and unbiased understanding of structure and composition. Standard deposition techniques for the underlying building blocks restrict possible candidates: Thermal evaporation in vacuum (MBE, OMBE) is limited to volatile substances. Solution based techniques such as drop casting, spin coating or inkjet printing are versatile but often lack purity and quality.

Electrospray ionization (ESI) combined with mass selection and soft-landing of molecules unravels the vast potential of large, reactive or bio-relevant building blocks. The pool of possible molecules spans a wide spectrum from small organic molecules, over graphene nanoribbons (GNRs) up to several kilo- and megadalton proteins, DNA, but also inorganic clusters and larger nanoparticles may be possible.

In-line with this, we present an UHV ion beam deposition device and its functionalities. Deposited layers are analyzed via STM. The main body of the device contains RF-driven ion guides with high transmission (>80% efficiency). A digital square-wave quadrupole mass filter (dQMF) provides virtually unlimited m/z-range. The footprint is benchtop in size, 0,5 x 1 m.

On the thermodynamics and kinetics of graphene growth on Cu and the properties of the synthesized material

Sebastian Günther, NAT School

Abstract:

We summarize our understanding of the chemical vapor deposition (CVD) of graphene on Cu by thermal decomposition of methane. It includes the measurement of the reaction entropy and enthalpy in comparison with the known values of graphite. Having determined these values, we can predict in which CVD parameter regime single and few layer graphene is synthesized. Quantifying the deviation from thermodynamic equilibrium during CVD growth, we can predict the flake diameter increase per growth time with a precision better than 20% at synthesis pressures above 10 mbar when not deviating too much from equilibrium and a growth speed
< 1 cm/hour. In this case, graphene flake growth proceeds via the attachment of adsorbed carbon (C-ad) atoms which are pre-equilibrated with the reaction gas phase. The extremely low saturation coverage of C-ad during growth explains why graphene synthesis is so sensitive to carbon contaminations of the gas feed and the Cu support.

When reducing the total pressure during CVD synthesis, “rare” reaction events become important and the growth kinetics change: At pressures below 10 mbar, graphene growth is fed from a pre-equilibrated CH_2-ad phase at reduced energy barrier. This trend continues during synthesis at even lower pressure in the hot wall reactor as reported recently.

Although being able to synthesize single layer graphene at highest crystalline quality, the properties of the synthesized graphene strongly depend on the treatment of the Cu foil prior and after synthesis. The well-known SiO release from the quartz tube reactor wall in a reductive atmosphere at high temperature leads to the Si enrichment of the used Cu support. Usually, the Si is dissolved in the Cu bulk and does not play a role at all, but oxygen exposure at $T>250$ °C can trigger Si segregation and conversion to silicon oxide at the graphene-Cu interface. Since Si acts as a scavenger of adsorbed oxygen, oxidation of the synthesized Cu is prevented which makes the graphene film seemingly chemically resistant. The effect is difficult to monitor and has been overlooked until now. In fact, many synthesis recipes rely on the formation of an intercalated surface Si oxide without knowing its existence. Since intercalated silicon oxide decouples graphene from the Cu support, it affects the electronic properties of the synthesized material.

Synthesis on Less Reactive to Inert Surfaces

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A key milestone in the field of On-Surface Synthesis (OSS) is the development of generic protocols for covalent coupling on inert surfaces. Typically, metal surfaces are used in OSS, but their strong interactions distort the intrinsic properties of the synthesized nanostructures and therefore compromise their applicability. Inert surfaces, on the other hand, preserve the nanostructures' unique properties, but present challenges during synthesis: In my contribution, the realization as well as the advantages and disadvantages of two different approaches to synthesis on less reactive to inert surfaces will be discussed: **(1)** partial passivation of metal surfaces and **(2)** annealing in a noble gas atmosphere.

(1) Coinage metal surfaces are readily passivated by iodine. However, depending on the exposure to iodine vapour, the iodine layers may not completely passivate the metal surface, leaving a residual reactivity sufficient to drive dehalogenative Ullmann-type couplings. Using a tetra-thiophine precursor, we demonstrate the synthesis of remarkably robust, electronically conjugated organogold networks on Au(111). The network regularity is significantly improved on iodine-passivated Au(111) compared to pristine Au(111). This is partly explained by the iodine-mediated reversibility of the otherwise strong C-Au-C organogold bonds.

(2) For the unfavourable but unfortunately common combination of high activation energies for coupling and low desorption energies, thermal coupling on inert surfaces is not feasible because the reactants simply leave the surface before coupling during annealing. Performing the annealing step in a noble gas atmosphere instead of a vacuum can decisively alter this kinetic competition in favour of coupling. Using 1,3,5-tris(4-mercaptophenyl)benzene (TMB) on graphite, we show that annealing in ~1.0 bar of argon yields covalently thioether-linked molecular fractals known as Sierpinski triangles. However, the kinetics is critical, as this protocol only works at ultra-slow heating rates, about two orders of magnitude lower than normal. The feasibility of the same synthesis protocol on even more weakly interacting graphene surfaces provides evidence that desorption into the argon-atmosphere becomes a diffusion-limited process.