O 45: Focus Session: Scanning Probe Microscopy with Quartz Sensors I

Atomic Force Microscopy (AFM) was quickly adopted in science and engineering, but it took a while until the field of surface could benefit from it. 2023 marks the 25th anniversary of the introduction of the qPlus sensor. This stiff and self sensing force sensor made from quartz that often uses an etched metal tip as known from scanning tunneling microscopy (STM) replaced the silicon cantilever and allowed new types of experiments and new domains of precision. Scientists used it to resolve the structure of organic molecules with atomic resolution, to obtain subatomic spatial resolution, to image spin structures and spin lifetimes, to measure lateral forces, to detect tiny water molecules, to image oxides and other insulating surfaces with atomic resolution. Operation in ambient conditions, ultrahigh vacuum (UHV), low (4 K) and ultralow temperatures (10 mK) and in high magnetic fields as well as in an electrochemical cell was demonstrated.

Organizer: Franz Giessibl (U Regensburg)

Time: Wednesday 10:30–12:30 Location: CHE 89

O 45.1 Wed 10:30 CHE 89

The genesis of the qPlus sensor — •Franz Giessibl — Institute of Experimental and Applied Physics, University of Regensburg, Universitätsstraße 31, 93053 Regensburg

In 1985, Gerd Binnig found exile from the STM frenzy at IBM Rüschlikon by a one year move to Stanford, the heart of silicon valley, and built the first atomic force microscope (AFM) together with Christoph Gerber and Calvin Quate [1]. Therefore, it is not surprising that the core of all AFMs, the cantilever, was soon micromachined from Si. Even the first successful imaging of Si 7x7 relied on piezoresistive Si cantilevers in the frequency modulation mode, albeit at an insanely large oscillation amplitude of 34 nm [2]. Benchmarking, widely used in management consulting, led to the conviction that quartz tuning forks with their utmost frequency stability would be a promising alternative. The phantastic frequency stability of the quartz forks used in Swatch watches and the realization that their stiffness allows sub-Angstrom oscillation amplitudes led to the invention of the qPlus sensor. Its stability, small amplitudes and low noise soon enabled subatomic resolution by AFM [3]. While qPlus sensors are standard in vacuum today, it is open if widespread application in ambient or liquid environments will become attractive, although atomic resolution has been demonstrated [4]. [1] G. Binnig, C.F. Quate, C. Gerber, Phys. Rev. Lett. 56, 930 (1986). [2] F.J. Giessibl, Science 267, 68 (1995). [3] F.J. Giessibl, S. Hembacher, H. Bielefeldt, J. Mannhart, Science 289, 422 (2000). [4] D.S. Wastl, A.J. Weymouth, F.J. Giessibl, Phys. Rev. B 87, 245415 (2013).

Topical Talk O 45.2 Wed 10:45 CHE 89

Single-molecule reactions performed and characterized using atomic force microscopy — •Leo Gross — IBM Research Europe - Zurich

Selective and reversible bond formation and dissociation can be controlled by tip-induced reduction-oxidation reactions on a surface. Molecular rearrangements leading to different constitutional isomers are selected by the polarity and magnitude of applied voltage pulses from the tip of a combined scanning tunneling microscope (STM) / atomic force microscope (AFM) [1].

Elusive molecules can be created and studied, such as cyclocarbons, i.e., molecular sp1 hybridized carbon allotropes [2] and molecules with high-spin ground states [3,4]. Moreover, insulating substrates allow probing charge states [5] and excited states [6].

References:
[1] F. Albrecht et al. Science. 377, 298-301 (2022).
[2] K. Kaiser et al. Science. 365, 1299-1301 (2019).
[3] N. Pavliček, et al. Nat. Nano. 12, 308-311 (2017).
[4] S. Mishra et al. ACS Nano. 16, 3264-3271 (2022).
[5] S. Fatayer et al. Science. 365, 142-145 (2019).
[6] S. Fatayer et al. Phys. Rev. Lett. 126, 176801 (2021).

O 45.3 Wed 11:15 CHE 89

On surface reaction of azaTrux molecules on Au (111) — •Outhmane Chahib[1], Jung-Ching Liu[1], Chao Li[1], Xunshan Liu[2], Uli Aschauer[2], Silvio Decurtins[2], Shi-Xia Liu[2], Ernst Meyer[1], and Rémy Pawlak[1] — [1]Department of Physics, University of Basel, Klingelbergstrasse 82, 4056 Basel, Switzerland — [2]Department of Chemistry and Biochemistry, University of Bern, Freiestrasse 3, 3012 Bern, Switzerland

One promising way to miniaturize electronic devices is to use "bottom-up" techniques, where functional organic molecules acting as elementary nanometer-sized "building blocks" are assembled or reacted on surfaces. Here we explore the on-surface reaction f 7,12-dibromo-5H-indeno[1,2-a]indolo-[3,2-c]carbazol-15(10H)-one molecules (AzaTrux) on the Au(111) surface into graphene nanostructures. Structural and electronic properties of nanostructures are characterized by scanning tunneling microscopy (STM) and atomic force microscopy (AFM) with CO-terminated tips. Using force spectroscopy, we further probe the donor-acceptor character of these nanostructures.

O 45.4 Wed 11:30 CHE 89

A two dimensional array of radical molecules on Pb(111) — Jung-Ching Liu[1], Chao Li[1], H. Chen[2], Ping Zhou[3], Xunshan Liu[3], Ulrich Aschauer[3], Silvio Decurtins[3], Shi-Xia Liu[3], Wulf Wulfhekel[2], Ernst Meyer[1], and •Rémy Pawlak[1] — [1]University of Basel, Basel, Switzerland — [2]Karlsruhe Institute of Technology, Karlsruhe, Germany — [3]University of Bern, Bern, Switzerland

The assembly of molecules to form a quantum dot array is of interest for quantum computing with the highest areal density. In this contribution, we show the supramolecular assembly of 4,5,9,10-tetrabromo-1,3,6,8-tetraazapyrene (TBTAP) molecules on superconducting Pb(111), self-organized in neighboring rows of radicals and neutral molecules [1]. By triggering a local field with a STM/AFM microscope at low temperature, we show that individual occupied molecules can be discharged efficiently, revealing Coulomb rings in spatial dI/dV maps. Charged molecules host spin 1/2, which is validated by dI/dV spectroscopy with μeV resolution through the observation of a pair of in-gap Yu-Shiba-Rusinov (YSR) states in the superconducting gap. The unpaired electron cloud extends spatially over the entire molecule and interacts with neighbouring electrons, resulting in the formation of YSR bands along the entire molecular domain. [1] J.C. Liu et al. submitted.

O 45.5 Wed 11:45 CHE 89

Self-Assembly Study of 1,2,10,11,12,14-hexafluoropentacene on a Au(111) surface by HR-AFM — •Miguel Wiche[1], Maximilian Dreher[2], André Schirmeisen[1], Gregor Witte[2], and Daniel Ebeling[1] — [1]Institute of Applied Physics, Justus Liebig University Giessen, Germany — [2]Fachbereich Physik, Philipps-Universität Marburg, Germany

The electronic properties of 2D organic materials highly depend on the orientation of the molecules inside the molecular thin film. For designing new materials with tailored functionality, it is important to understand the self-assembly processes of the individual molecular building blocks on surfaces. For example, the role of intermolecular halogen bonds for the molecular arrangement is not well understood. A powerful tool to investigate assembly processes in a step-by-step fashion is the bond imaging AFM method, which is based on operating qPlus sensors under UHV conditions at low temperatures with CO-functionalized tips. Here, the onset of the self-assembly process of individual partially fluorinated 1,2,10,11,12,14-hexafluoropentacene molecules on Au(111) is studied. Therefore, the molecules are first evaporated onto a cold surface (around 6K) where molecular diffusion is negligible. The formation of small clusters with closely packed molecules all facing in the same direction is induced by subsequent heating steps to temperatures up to 50K. At higher temperatures (80-300K) also larger islands form. After each heating step, the sample

is cooled down to 5K for determining the precise bonding angles and length of the intermolecular F···H contacts via bond imaging AFM.

O 45.6 Wed 12:00 CHE 89

On-surface synthesis of PAHs by strain and the concerted motion of adatoms. — •Benjamin Mallada[1,2], Bruno de la Torre[1,2], Jesus I. Mendieta-Moreno[2], Adam Matej[1,2], Mikulas Matousek[3], Jiri Brabec[3], Libor Veis[3], Timothee Cadart[3], Martin Kotora[4], and Pavel Jelinek[1,2] — [1]Czech Advanced Technology and Research Institute (CATRIN), Olomouc, Czech Republic — [2]Institute of Physics, Czech Academy of Sciences, Prague, Czech Republic — [3]J. Heyrovsky Institute of Physical Chemistry, Prague, Czech Republic — [4]Department of Organic Chemistry, Charles University, Prague, Czech Republic

The kinetic control of the synthesis of polycyclic aromatic hydrocarbons (PAH) is one of the most desired features in organic synthesis. In this work, we report the synthesis and characterization by STM/nc-AFM of several PAHs from one single precursor in which two different kinetic-driven mechanisms control the possible products at high temperatures. In the first mechanism, we show that the surface-induced mechanical constraints on a strained helical reactant leads to the synthesis of planar objects with non-benzenoid rings. In the second mechanism, the chemical pathway is mediated by an unusual C-C bond cleavage of the helical reactant mediated by the concerted motion of individual gold adatoms. These observations, supported by DFT and state-of-the-art QM/MM calculations, render a scenario where the molecular internal stress and the adatoms' role enable routes to the kinetic control of selected chemical reactions.

O 45.7 Wed 12:15 CHE 89

Monitoring of molecular configurations in SPM-based molecular manipulation — Joshua Scheidt[1], Alexander Diener[1], Michael Maiworm[2], Klaus-Robert Müller[3], Rolf Findeisen[2], Kurt Driessens[4], F. Stefan Tautz[1], and •Christian Wagner[1] — [1]Peter Grünberg Institut (PGI-3), Forschungszentrum Jülich, Germany — [2]Control and Cyber-Physical Systems Laboratory, Technische Universität Darmstadt, Germany — [3]Machine Learning Group, Technische Universität Berlin, Germany — [4]Data Science and Knowledge Engineering, Maastricht University, The Netherlands

Molecular manipulation with the SPM tip as an actuator allows creating a wide variety of molecular junction configurations. Unfortunately, the precise atomic locations in such a junction, which strongly impact its mechanical and electronic properties, cannot be observed directly. Here, we present and benchmark an approach that enables such a configuration monitoring. It overcomes the most important challenges: the need for accurate yet fast simulations, the disparity between scalar observation quantities like a force gradient and a high-dimensional unknown molecular configuration, the vast configuration space to be searched, and the need to operate on the few-minutes time scales of typical experiments. This is achieved by combining a finite state automaton to store and rapidly access the results of atomistic molecular simulations, and a particle filter to search for likely manipulation trajectories, given an input sequence of observations. We are able to assign systematic differences in generic features in force gradient data to well-defined atomic configurations for the first time.