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Imaging and manipulation of molecules on surfaces with scanning probe methods

Introduction

Since the invention of scanning tunneling microscopy (STM) [1] in 1982 and the subsequent development of atomic force microscopy (AFM) [2], scanning probe techniques have become essential tools across condensed matter physics and surface science. These techniques enable atomically resolved imaging and spectroscopy that have advanced our understanding of quantum phenomena and provide quantitative insight into the chemical and structural properties of molecules and materials on surfaces. Studies range from characterizing surfaces and adsorbed molecules of fundamental interest [3, 4] to clarifying the composition of real-world systems like the solid components of petroleum [5], soot formation [6], and organic compounds found in meteorites [7]. Recent developments open up perspectives for rapid molecular prototyping and the construction of artificial quantum systems.

Electronic structure in STM

In conventional constant-current STM images, molecules appear with well-defined shape, as illustrated for the hexagonal heterocycloarene $C_{102}N_6H_{30}$ in Figure 1a. While it is tempting to interpret these images as direct pictures of molecular geometry, the image contrast is determined not only by the atomic positions but, more fundamentally, by the electronic structure of the sample. This becomes clear in the framework of the Tersoff–Hamann model, which assumes a tip wave function of s-wave symmetry. Within this approximation, the tunneling current I_t is proportional to the local density of states (LDOS) of the sample, integrated over the energy range between the Fermi level E^S_F and the bias-shifted energy E^T_F (Figure 2b). Thus, an STM topograph is an energy-integrated map of the LDOS, rather than a simple "height profile". By varying the applied bias voltage V_{bias}, the contribution of different electronic states can be selected. Measuring the differential conductance (dI/dV) as a function of V_{bias} yields scanning tunneling spectra that reflect the LDOS at the probed site. When V_{bias} is tuned to the energy of a particular molecular orbital, constant-current dI/dV images (commonly called "orbital images") show how the LDOS associated with that orbital is distributed in space. Figure 1e shows such images for the HOMO and LUMO of the cycloarene.

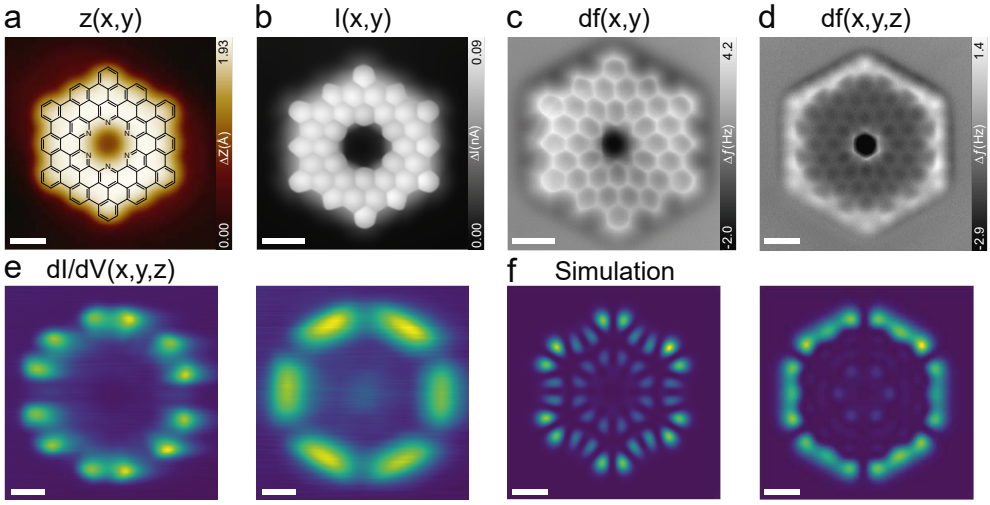

Fig. 1: Scanning probe microscopy (SPM) investigation of the heterocycloarene $C_{102}N_6H_{30}$ on a Au(111) surface. a) Constant-current STM, b) bond-resolved STM, c) bond-resolved AFM, d) constant-current AFM, e) differential conductance maps related to the density of states of HOMO and LUMO of the molecule, and f) corresponding simulations of the conductance maps. The scale bars indicate a length of 0.5 nm.

Tip functionalization

The exceptional mechanical stability of low-temperature STM enables deliberate tip functionalization with small molecules, a now-established method to enhance both spatial resolution in images and energy resolution in tunneling spectra. The most widely used case is termination with carbon monoxide (CO): the p-like frontier orbitals of the CO modify the tunneling matrix elements, making the STM signal sensitive to lateral variations of the local density of states [8]. This additional sensitivity explains the submolecular contrast of CO-tip images. Corresponding simulations that include this derivative-like effect (see Figure 1f) reproduce the experimentally observed orbital images with high accuracy.

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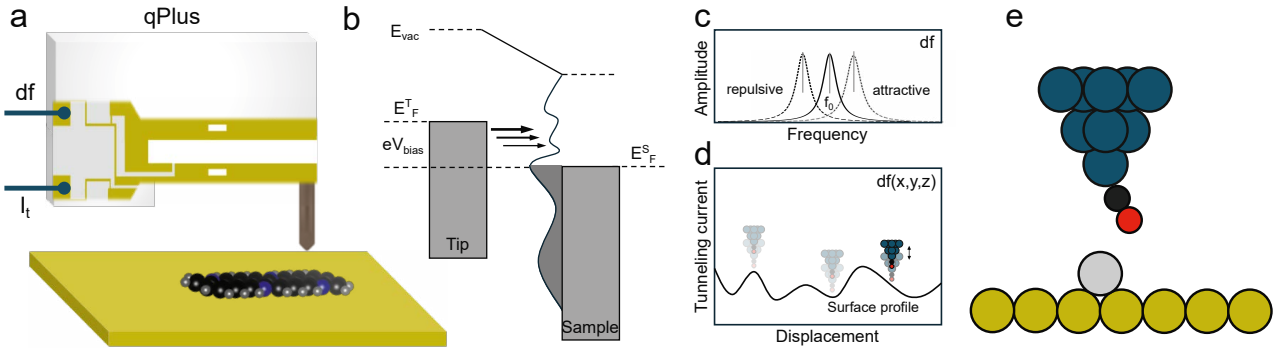

Fig. 2: Technical aspects of scanning probe microscopy. a) Experimental setup with qPlus tuning fork sensor. b) Electronic structure imaging in STM. Visualizations of c) the frequency modulation AFM mode, d) the constant-current AFM mode, and e) the interaction of a CO-functionalized tip with an atom on the surface.

Geometric structure

At small tip-sample distances, a CO-functionalized tip can be deflected by lateral forces and bend away from the surface, as illustrated in Figure 2e. According to the probe-particle model [9], this mechanical response leads to a geometric-type contrast with exceptionally high spatial resolution. In constant-height mode, the resulting "bond-resolved" STM clearly reveals intramolecular features: as shown in Figure 1b, even the individual benzene rings within the cycloarene are clearly resolved.

Non-contact AFM

Low-temperature operation with a functionalized tip on a tuning-fork qPlus sensor [10] (Figure 2a) enables bond-resolved AFM imaging (Figure 1c). Unlike conventional microcantilevers, this rigid quartz tuning fork combines a high resonance frequency with small oscillation amplitudes, making it ideally suited for frequency modulation AFM (Figure 2c). Its piezoelectric properties allow self-sensing, eliminating the need for laser readout and thus permitting operation in compact microscopes without optical access. AFM signal and tunneling current can be recorded simultaneously, allowing for combined access to geometric and electronic structure. This also enables other scanning modes like constant-current or constant-dI/dV AFM modes (Figures 2d, 1d), which further enhance bond-resolved imaging, especially for nonplanar molecules.

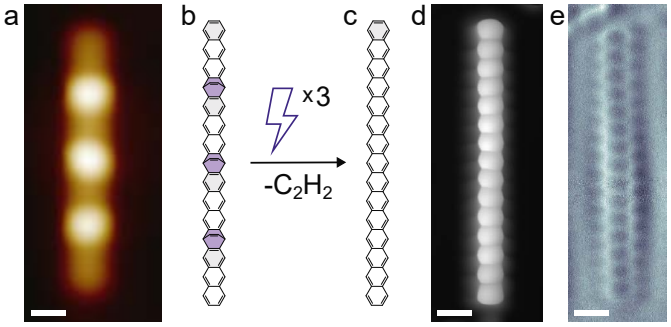

Fig. 3: Synthesis by single-molecule manipulation [3]. a) STM image and b) chemical structure of a molecular precursor that was prepared in solution and vapor deposited onto a Au(111) surface. c) Chemical structure, d) bond-resolved STM image, and e) AFM image of the pentadecacene prepared by multistep STM-tip manipulation. The scale bars indicate a length of 0.5 nm. Modified from J. Am. Chem. Soc. 2025, 147, 6, 4862–4870, under the Creative Commons CC BY 4.0 license.

Molecular synthesis by tip manipulation

Controlled manipulation in scanning probe microscopes has recently become a powerful tool for atomically precise molecular synthesis. The tip can be used to move adsorbate molecules directly or to induce site-specific reactions by applying short bias pulses that break (or form) selected bonds. Figure 3 visualizes such a tip-enabled synthesis of a long acene molecule, which is inaccessible by solution synthesis due to its open-shell polyradical character. Here, targeted bias pulses remove protecting groups from the molecular precursor, enabling full conjugation in the π-electron system. These and other recently synthesized molecules like cyclocarbons [4] are of fundamental interest and represent early steps toward the atomically-precise bottom-up fabrication that was envisioned by Richard Feynman in 1959 [11]. Surfaces serve as ideal platform to investigate the geometric, (opto-)electronic, and magnetic properties of single molecules synthesized by tip manipulation and thereby also benchmark their suitability for applications.

Beyond Feynman's dream

The recent advances toward bottom-up manufacturing let us envision fast molecular prototyping. The aid of artificial intelligence-based automation of tip preparation and scanning probe methods [12], identification of molecules [13], and prediction of molecular properties [14], promises to accelerate progress well beyond the vision first outlined by Feynman.

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QUOTES

"Science doesn't always go forwards. It's a bit like doing a Rubik's cube. You sometimes have to make more of a mess with a Rubik's cube before you can get it to go right. You build up this picture of what there is and you believe it to be true and you work with this picture and you refine it but sometimes you have to abandon the picture. Sometimes you discover the picture you thought you had, that everybody thought we had, actually turns out to be wrong."

Jocelyn Bell Burnell (radio astronomer)

Dr. Sabine Wenzel

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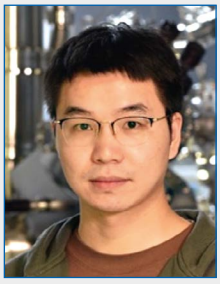
Sabine Wenzel studied physics at TU Darmstadt (BSc, 2014) and Leiden University, The Netherlands (MSc, 2017). She received her PhD under supervision of Prof. Irene M.N. Groot at the Leiden Institute of Chemistry performing microscopy and spectroscopy on model catalyst surfaces in gas environments. As a postdoctoral researcher at the Institute for Quantum Nanoscience in Jülich (2021-2024), she characterized 2D materials with low-temperature scanning probe methods. Her recent junior research group at Marburg University focuses on the on-surface synthesis of molecular systems on oxidic surfaces.

Dr. Zilin Ruan



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Zilin Ruan received his BSc in Material Physics from Wuhan Institute of Technology in 2016 and completed his PhD in 2022 under Prof. Jinming Cai at Kunming University of Science and Technology, focusing on synthesis and characterization of surface nanostructures by scanning probe spectroscopy. Since 2022, he has been a postdoctoral researcher in the Gottfried group at University of Marburg, Germany. In 2023, he was awarded a two-year Alexander von Humboldt Postdoctoral Fellowship for work on single-molecule manipulation, on-surface synthesis, and graphene nanostructures.

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J. Michael Gottfried is Professor of Physical Chemistry at Philipps-Universität Marburg. He studied Chemistry and Physics in Darmstadt, St. Andrews, and Berlin, earning his PhD in 2003 with K. Christmann at Freie Universität Berlin. After postdoctoral work with C.T. Campbell at University of Washington and habilitation with H.-P. Steinrück in Erlangen, he became professor in Marburg in 2011. His research centers on surface physical chemistry. He received major awards and an ERC Synergy Grant in 2022.