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The quest for pushing the resolution in scanning probe microscopy forward to the atomic scale has been a driving factor since the invention of the scanning tunneling microscope (STM) [1] and the atomic force microscope (AFM) [2]. Recently, noncontact AFM was used to resolve the structure of an individual molecule with atomic precision [3]. A crucial factor to increase the lateral resolution was to use a functionalized tip, which is a deterministic chemical modification of the last atoms of the scanning probe tip. The tip can be functionalized by atomic manipulation, that is picking up a specific adsorbate from the sample surface [4, 5]. Importantly, the atomic/molecular functionalizations yield the predominant force contributions for the interaction on the atomic scale [6]. The most widely used tip functionalization for high-resolution AFM to date is a single CO molecule [3].

For any interpretation of AFM data, understanding of the contrast mechanism is crucial. At first glance, the atomically resolved AFM images as the one shown in Fig. 1a being similar to the molecular structure, suggest that the contrast simply reflects the geometry of the molecule. However, the imaging mechanism is far from being simple. First, the AFM signal is composed of several different types of interactions, such as electrostatic forces, van der Waals attraction, chemical bond formation, and Pauli repulsion. Additionally, as these forces act on very different length scales, different parts of the tip and sample structure may contribute to the imaging process. Density functional theory (DFT) is a crucial tool to separate different force contributions in order to understand the imaging mechanism. It could be shown that Pauli repulsion is responsible for the atomic contrast observed in AFM images and the long-ranged van der Waals and electrostatic forces compose the attractive background [6].

An important effect to account for are possible tip relaxations. Specifically, tilting of CO and other terminations occur because of lateral forces, which critically affects the image contrast [7 - 9]. CO tilting leads to a sharpening of the bonds and distorts the apparent molecule structure, which can also be exploited to differentiate the bond order of individual bonds in molecules [7].

To study compounds on a single molecule basis with scanning probe techniques requires to work at ultrahigh vacuum and low temperatures (typically 4 K). As a sample we use a Cu(111) single crystal partly covered by micrometer-sized two-monolayer thick NaCl islands. In recent years, such ultrathin insulating films on metal substrates have gained appreciable attention as templates for the study of individual adsorbates [10 - 12]. This attention stems from both the decoupling of the adsorbate electronic states from the metal substrate and the weak adsorbate-film interaction, which

makes it possible to study single molecules and atoms close to their native state.

The identification of molecular structures is an important emerging application of high-resolution molecular imaging by AFM with functionalized tips. Recently, AFM was used in combination with conventional techniques (i.e nuclear magnetic resonance and mass spectrometry) for the structure elucidation of natural compounds [13, 14] and to identify reaction products formed by on-surface chemistry [15] and by atomic manipulation [16]. In the following we briefly review two of our recent studies: (i) an example where we analyzed a mixture of molecules present in petroleum [17] and (ii) a sequence of single-molecule reactions induced by atomic manipulation [18].

A strength of AFM is that single molecules can be addressed. This renders possible to investigate also samples that are mixtures of molecules and to identify their structures individually. Petroleum is probably the most prominent natural mixture and one of the most complex materials encountered with possibly over 100,000 distinct chemical constituents [19]. A very enigmatic fraction of petroleum is asphaltene that is defined by a solubility classification that covers essentially the solid component of crude oil. Because of their

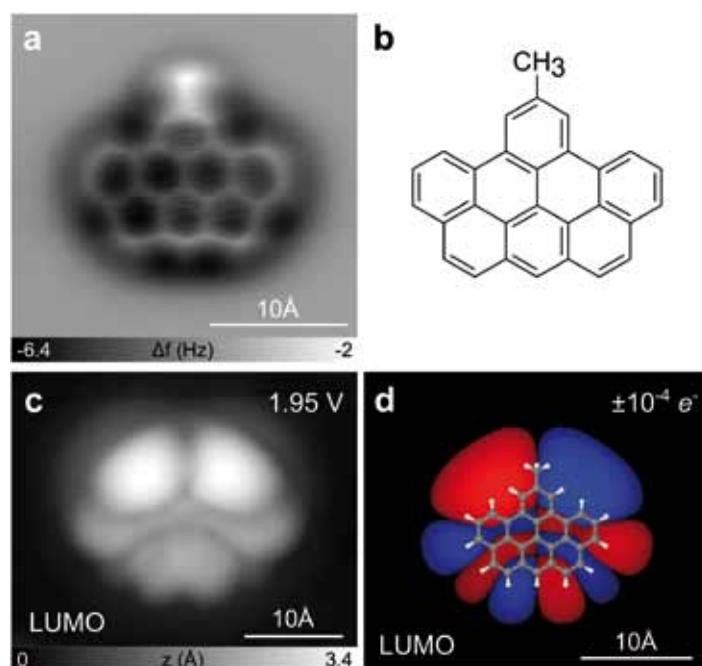


FIG. 1. *Asphaltenes*. **a**: AFM image of an asphaltene molecule revealing the structure. **b**: Structure hypothesis from **a**. **c**: STM orbital image of the lowest unoccupied molecular orbital (LUMO). **d**: Density functional theory calculation of the LUMO of **b**. Adapted with permission from Schuler et al. [17]. © 2015 American Chemical Society.

complexity, asphaltenes are posing an exceptional challenge for structure analysis. Although immense financial efforts are taken to learn about this substance as a matter of its economic relevance, even the most basic properties such as the mean molecular weight or molecular architecture have been under debate since years.

In our approach we used high-resolution AFM and STM to measure the atomic structure [3] and molecular orbitals [12] of individual asphaltene molecules. In Fig. 1a an AFM image of a molecule found in the asphaltene mixture is shown. In simple cases like here we can directly assign its structure from such an image (see Fig. 1b). When the molecule is located on an insulating NaCl island it is possible to access its frontier molecular orbitals by tuning the sample voltage such that electrons tunnel resonantly through the lowest unoccupied molecular orbital (LUMO) or the highest occupied molecular orbital (HOMO). A STM orbital image of the LUMO resonance of the molecule in Fig. 1a is shown in Fig. 1c. STM orbital imaging provides valuable complementary information about the molecule structure. The orbital images reflect an isosurface of the respective orbital as depicted in Fig. 1d. In this way the orbital images provide an independent cross-check of the structure assignment.

In the more than 100 atomically-resolved AFM images of individual asphaltene molecules we observed a tremendous diversity of different structures. The asphaltenes consist of a central aromatic core composed of generally one and sometimes a few polycyclic aromatic hydrocarbons and some aliphatic side-groups attached that can vary in their abundance and length depending on the sample origin and possible hydroprocessing. From such measurements, one can learn about the mixture characteristics and potentially gain a better understanding of physicochemical processes involved in petroleum processing.

The demonstrated structure elucidation of mixtures could also be viewed as a paradigm shift for the development of new molecules, as it makes the time-consuming synthesis and purification of tailored molecules redundant. Rather, many molecules can be screened in a single preparation.

A focal interest in chemistry is not only to analyze reaction products but also to understand reaction pathways. Reactive intermediates are involved in most chemical transformations. However, their characterization is a great challenge

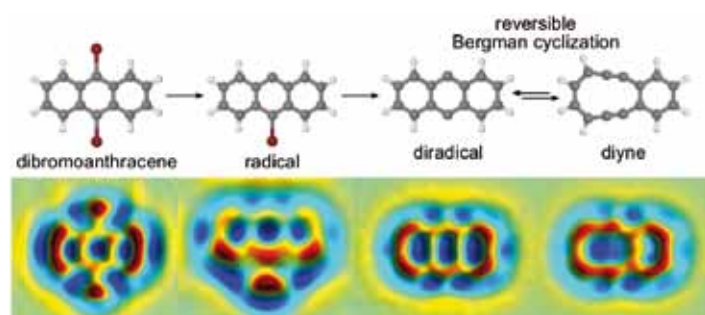


FIG. 2. Bergman cyclization. Top row: Chemical structures of the reaction products formed by successive STM-induced debromination of dibromoanthracene and subsequent retro-Bergman cyclization. Bottom row: AFM images of the respective reaction intermediates and products. Reprinted from Schuler et al. [18] with permission from Macmillan Publishers Ltd: *Nature Chemistry*, © 2015.

because of their short lifetime and high reactivity. The thin insulating NaCl film allows us to stabilize these reactive intermediates at cryogenic temperatures [16]. Still, their reactivity remains preserved even at low temperatures as proven by the ability to undergo different on-surface reactions triggered by atomic manipulation [16].

We could demonstrate the sequential derivation of diene by three single-molecule reactions starting from dibromoanthracene (DBA) by means of atomic manipulation (see Fig. 2). The reaction intermediates and product could be identified and characterized by atomic resolution AFM measurements and STM orbital imaging that are compared with DFT calculations. Starting from DBA, two Br atoms could be cleaved from the molecule by applying voltage pulses with the tip to form a *para*-aryne diradical. In a last step, the diradical could be transformed into a highly-strained diene molecule, which represents a so-called retro-Bergman cyclization. Interestingly, this reaction was reversible and we could trigger switching between diradical and the two possible diene topomers, constituting a tri-state molecular switch. Thus, we demonstrate the creation and annihilation of an intramolecular C - C bond by atomic manipulation. DFT calculations reveal that upon this switching also the spin multiplicity is switched between a spin-singlet (diene) and a spin-triplet (diradical) ground state [18], implying a change of the molecule's reactivity, optical and magnetic properties.

High-resolution noncontact-AFM and STM are valuable tools to gain insights into matter on the atomic scale. Specifically, we exploited the contrast enhancements provided by functionalized tips. The opportunity to study the structure of molecules and their properties on a single-molecule level offers exciting new ways to explore atomic-scale processes in molecular systems.

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