Translation and rotation of a haloaromatic thiol

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Abstract

Lateral manipulation of a halosubstituted aromatic thiol (p-bromothiophenol) by use of a scanning tunneling microscope (STM) operated at cryogenic temperatures is always associated with the alignment of the molecule in the translation direction. Tip-height traces acquired during lateral manipulation yield further insight into the dynamic behavior of the molecule. CO-functionalization of the STM tip renders imaging conditions more stable by reducing the attractive interaction between the tip and the thiol.

1. Introduction

Thiols, and especially aromatic thiols, are the central building block of most systems for molecular electronics. Thiol groups can anchor an organic molecule securely on the surface of a coinage metal. In conjunction with an aromatic backbone within the molecule, the thiol–substrate bond is sufficiently conductive for the observation of switching characteristics [1], of charging of the molecule [2] and of redox chemistry [3]. Lateral manipulation of individual adsorbates by the tip of a scanning tunneling microscope (STM) is the most precise way of positioning atoms and molecules on metallic substrates. It was first realized in the group of Eigler using Xe atoms on a Ni(110) surface [4]. Meanwhile, the technique has been extended to a wide variety of systems including relatively large fullerenes [5,6] and molecular clusters [7], medium-size lander molecules [8] and small substituted benzenes [9] as well as metal atoms [10]. Atomic precision is possible in fairly extended structures [11] and efforts are underway to automatize this process [12]. In conjunction with multi-tip designs currently developed for data storage [13], STM-based fine-tuning of crucial areas of functional structures may be a common procedure of future nanotechnology.

2. Experimental

We present experiments elucidating the elementary steps of the lateral translation of a substituted aromatic thiol, namely p-bromophenylethiolate (BPT) (Fig. 1a), on Cu(111). The mobility of thiols on Au(111) has significant potential for causing failure in molecule electronic devices and the increased strength of the S–Cu bond compared to the S–Au bond may increase the use of Cu(111) as a substrate material. We chose a bromo-substituted thiol because bromine is a good leaving group. Bromo-substitution allows both wet-chemical conversion of BPT to a broad range of products and STM-based activation similar to iodo-substitution [14]. During lateral manipulation in constant current mode, we observe hopping patterns similar to metal atoms and non-thiol molecules [9,10]. In contrast to previous work, we also find a strong dependence of the molecular behavior on the manipulation direction with respect to the molecular axis: BPT only follows the tip when the tip addresses it by the bromine side; during lateral manipulation the molecule always rotates, so that the sulfur atom trails behind.
sample to $2 \times 10^{-9}$ torr for 30 s. We abstracted the hydrogen from the thiol group similar to the abstraction of hydrogen from dichlorothiophenol described in [15].

3. Results

BPT appears as an elliptical protrusion of \( \approx 0.67 \) Å height, which points towards an apparent dip in the substrate (Fig. 1b). This dip reflects the adsorption position of the sulfur atom and has a depth of \( \approx 0.07 \) Å. Sulfur generally appears as an indentation on Cu(111), quite similar to its oxygen homologue [16]. The bromine substitution site appears prominent in STM, which creates the overall elliptical shape of the molecule (Fig. 1b and c). There are a total of six equivalent surface orientations for the molecule adsorbed as shown in Fig. 1a. Three of these originate from the threefold symmetry of the substrate (i.e., 120° between orientations) and another set of three is generated by the inversion symmetry of the surface. The two sets of three orientations have an angle of 46° between them, i.e., there are 46° and 74° between them in an alternating fashion. Abstraction of the substituents of the aromatic ring (S or Br) is possible at a bias exceeding 2.5 V of either polarity.

Fig. 1c shows a series of lateral manipulation experiments. The molecule on the right is not addressed by lateral manipulation and serves as a reference. All manipulations utilize \(-100 \) mV of bias and a setpoint current of 3.5 nA, i.e., a setpoint resistance of 29 MΩ. This is a relatively high resistance for manipulation experiments, if compared to metal atoms [10], but it is well in line with data by Hla et al. [9] on diiodobenzene. Our lateral manipulations proceed at a tip speed of \( \approx 420 \) Å/s. The yellow arrows in Fig. 1c indicate the direction of manipulation; they are drawn at a lateral offset with respect to the actual tip path.

The sequence of images shows that lateral manipulation of BPT is a highly reproducible process. Evaluation of the final sites of the BPTs confirms that they are pulled across the surface by an attractive interaction with the tip. Moreover, lateral manipulation is found to rotate the molecule so that the bromine always points in the direction of the translation. Correspondingly, the sulfur, which anchors the molecule to the substrate, is dragged behind. This suggests that the tip primarily interacts with the bromine side of the molecule. Consequently, lateral manipulation does not only translate the molecule on the surface, it also aligns it with the movement trajectory.

The success of lateral manipulation depends on which portion of the molecule is addressed: if the tip is guided across the benzene ring or the bromine atom, the molecule can rotate itself towards the tip, strong attractive interaction occurs and the manipulation will be successful. However, if the tip is guided perpendicular to the molecular axis across the sulfur atom, no lateral manipulation is achieved (black arrow in Fig. 1c, 11). Similarly, if the tip is moved across BPT at a lateral offset of \( > 1 \) Å, then BPT can swing around the sulfur peg and the manipulation can be accomplished. We further corroborated the importance of the bromine atom for the lateral manipulation of BPT by performing similar experiments with \( p \)-chloro and \( p \)-fluoro substituted thiophenols. Neither of these compounds exhibits BPT’s facility of lateral manipulation.

Fig. 1. (a) This adsorption geometry of BPT on Cu(111) can be realized in six rotational orientations with the sulfur located at an fcc hollow site (as drawn) and in six further ones with the sulfur at an hcp hollow site. (b) 3D view of a BPT molecule on Cu(111) (65 pA, \(-200 \) mV). The small dip on the right corresponds to the sulfur adsite. (c) Sequence of images (65 pA, \(-200 \) mV) taken during the lateral manipulation (3.5 nA, \(-100 \) mV) of the BPT molecule on the left. The yellow arrows indicate the manipulation direction and are drawn at an offset with respect to the manipulation pathways, which always lead across the center of the molecule. The molecule marked x is not moved and serves as a reference. Tip pathways that follow the red and the black arrow (11) do not lead to molecular manipulation.
In order to better understand the lateral manipulation of BPT, we record the tunneling current and the tip height along the manipulation path before, during and after the manipulation. Fig. 2a shows a set of tip-height traces associated with a lateral manipulation as shown in Fig. 1c, 1). The setpoint current is 65 pA at −200 mV during imaging and 3.5 nA at −70 mV during manipulation. The vertical offset between the tip-height curves during scanning (blue) and lateral manipulation (red) is caused by the change in gap resistance. The first step of the red trace reflects the rotation of the bromine side of the BPT towards the incoming tip. Subsequently, the molecule rotates relatively smoothly around its sulfur anchor in order to follow the tip motion. Once rotation becomes insufficient to keep the bromine atom in close proximity to the tip, the molecule starts to follow the tip by hops of individual adsites distance (Cu–Cu distance \( \approx 2.5 \) Å).

The low corrugation of the red trace during rotation bears witness of the strong interaction of the Br with the tip apex compared to the substrate. Indeed, if a higher setpoint current is chosen, then the tip is prone to pick up BPT permanently. Fig. 2b shows the tip-height trace during a corresponding experiment. Pickup of the molecule extends the apparent length of the tip by \( \approx 3.5 \) Å.

Lateral manipulation can be made less facile (and, hence, imaging more stable), if a CO molecule is transferred onto the tip apex [16]. We find on our sample a contamination of <0.001 ML of CO molecules and identify them by transfer onto the tip as described in [16]. CO-tips image BPT identically to metal tips except for a \( \approx 10\% \) reduction in corrugation. We perform lateral manipulation with a CO-tip and find that the required tunneling current at constant voltage is three times higher than before CO-functionalization. The corresponding tip-height trace (Fig. 2c) shows steps that are \( \approx 3 \) Å high, much taller than BPT images with a bare (or CO-functionalized) tip. Also, the traces change between single and double hops in an irregular fashion. According to [16], the attachment of a CO molecule to the tip reduces the separation between the tip apex metal atom and the sample. Thus, we speculate that in the case of a CO tip the tunneling junction during lateral manipulation intermittently resembles a pickup of the molecule, whose permanent attachment to the tip is prevented by the passivating character of the CO adsorption.

4. Discussion

Having characterized the molecular motion, we wish to point out that the six rotational orientations, which BPT can attain while its sulfur atom is locked into the same hollow site, may be used for encoding information in a way that directly derives from the nanoscopic properties of the system, i.e., the registry between BPT
and Cu(1 1 1). A number of STM-based schemes have been proposed that are capable of encoding information on surfaces at unprecedented information densities. Yet, they generally extend macroscopic encoding methods (e.g., the absence or presence of hydrogen termination in patches of the sample similar to a punch card [18], order in a row of fullerenes similar to an abacus [4]) rather than utilizing features that are specific to the nanoscopic properties of the system. We set the STM tip to travel in a circle around a sulfur atom of a BPT at a radius corresponding to the S–Br distance. Fig. 2d shows the corresponding tip-height traces recorded before, during and after lateral manipulation. The total acquisition time for this sequence of readout of the molecular orientation, controlled modification of the orientation and renewed readout is ≈0.1 s. The six accessible orientations of BPT can encode almost the same information as three bits but use less than 2 nm². The speed of this read–write–read cycle is not impressive in comparison to current storage device and the low temperatures as well as precise control requirements render it not technologically practical at this point. Nevertheless, our experiments still show the potential of an encoding mechanism that naturally derives from the nanoscopic setup of the system. We use a combination of higher gap resistance and slow feedback in order to avoid lateral transfer of the molecule and to render the changes of rotational orientation of BPT better visible than in Fig. 2a.

5. Summary

In conclusion, we find that the lateral manipulation of p-bromophenylthiolate is facile as long as it is sterically possible to align the molecule with the direction of the tip movement. Modifications of the gap resistance or the chemical composition of the tip have a strong impact on the nanoscopic behavior of BPT during lateral manipulation.

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