Manipulation of azobenzene molecules on Au(111) using scanning tunneling microscopy

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We have manipulated single azobenzene molecules using several different techniques with a variable-temperature scanning tunneling microscope (STM). Isolated azobenzene molecules were adsorbed and manipulated on the Au(111) surface at low temperature ($T=34$ K). STM tip voltage pulses reversibly switched the azobenzene molecule between two stable orientational configurations. A sliding technique was used to move single azobenzene molecules between stable sites on the surface, enabling construction of molecular chains. Stable sites (i.e., molecular anchor points) were created on the Au(111) surface through STM tip voltage pulses.

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Molecular electronics promises a new generation of devices with potential advantages in speed and functionality.[1–3] "Bottom-up" fabrication using a scanning tunneling microscope (STM) tip has been pursued as one technique for creating prototype molecular structures and testing their properties. Various structures have been assembled and tested using this technique, including adatom structures,[4–7] porphyrin,[8–10] fullerene,[11] and other molecular assemblies.[12,13] These systems allow electronic, magnetic, and mechanical properties to be tuned at the nanometer scale. Azobenzene molecules are of particular interest for molecular manipulation because they offer the possibility of coupling optical excitations with mechanical degrees of freedom at the single molecule level. This arises from the fact that azobenzene consists of two phenyl rings joined by two double-bonded nitrogen atoms, and is known to transition between metastable *cis* and *trans* configurations when optically excited in solution.[14,15]

Here we demonstrate several different techniques for manipulating azobenzene molecules using an STM tip. The first involves rotational bistable switching of individual molecules anchored at defect sites on a Au(111) surface. The second involves lateral manipulation of individual azobenzene molecules via a tip-controlled sliding mechanism. The third technique involves the creation of stable molecular anchor sites on the surface via voltage pulsing of the STM tip.

We performed our measurements using a home-built variable-temperature ultrahigh vacuum STM (base pressure $<5\times10^{-11}$ Torr). All of our experiments were performed on a Au(111) substrate that was cleaned by repeated cycles of Ar-ion sputtering and annealing. Azobenzene molecules were leaked into the vacuum chamber and deposited onto the Au(111) substrate at room temperature. After azobenzene exposure, the sample was transferred to the STM which was operated between 34 K and room temperature. Tunneling currents were kept below 100 pA for stable imaging.

At low azobenzene coverages (<0.1 ML), we observe individual molecules anchored to "kinks" of the Au(111) reconstruction, as shown in Fig. 1. This is in contrast to the self-assembled parallel chain structures observed at higher azobenzene coverage.[16] The low coverage images in Fig. 1 were taken at a reduced temperature of 34 K to hinder lateral molecular diffusion. Single azobenzene molecules appear as pairs of bright protrusions, marking the phenyl rings of the molecule. The Au(111) herringbone reconstruction can be observed in the background as parallel pairs of slightly elevated surface ridges [traced by dashed lines in Fig. 1(a)]. Single molecules adsorb at the kink site of the herringbone reconstruction and orient outwards from the kink in either of two equivalent directions at ±30° to the direction bisecting the kink.

Using tip-induced voltage pulsing we are able to toggle individual azobenzene molecules between these two orientation states. This process can be seen for two azobenzene molecules (molecules 1 and 2) in Figs. 1(a)–1(e). Figure 1(b) shows the orientational change of molecule 2 after it has been subjected to a single 1 μs long, −3 V pulse (increased

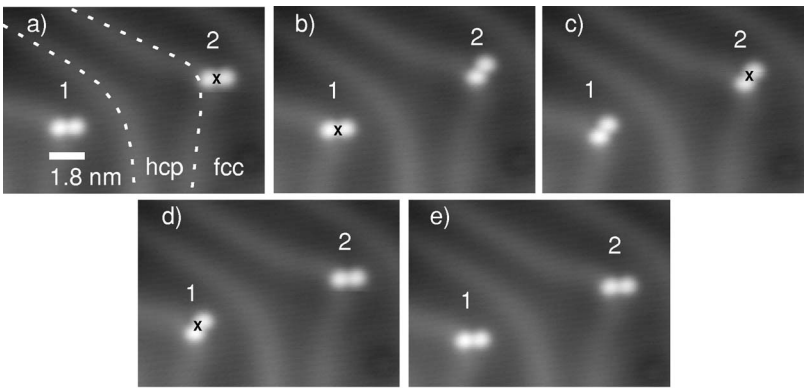

FIG. 1. A low temperature (T=34 K) STM manipulation sequence: isolated azobenzene molecules on the Au(111) surface are selectively and reversibly switched by STM tip voltage pulses. An "X" marks the position of the tip above a selected molecule just before a tip voltage pulse causes that molecule to rotate (as seen in each following image). The dotted lines in (a) trace the Au(111) herringbone surface reconstruction domain walls separating hcp and fcc domains. The imaging parameters are −1.25 V, 50 pA.

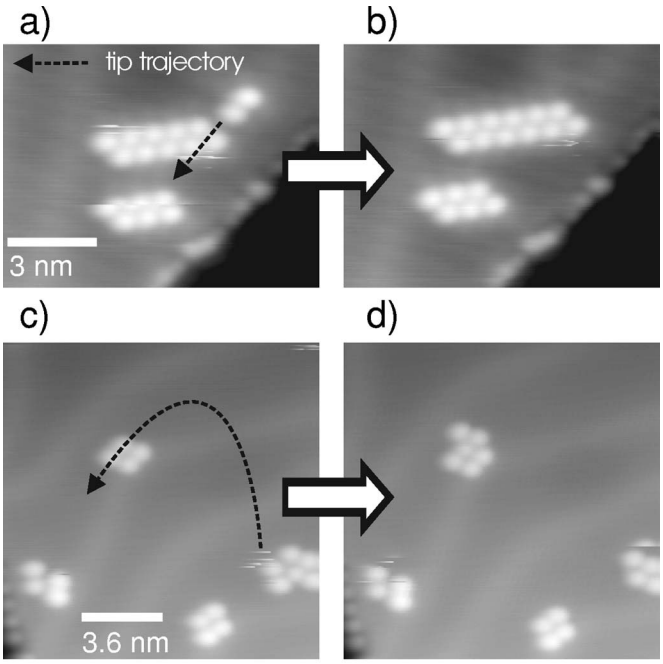

FIG. 2. Two low temperature (T=36 K) STM sequences demonstrating lateral manipulation of single azobenzene molecules enabling molecular chain construction. Dotted lines indicate path of STM tip during manipulation. (a) and (b) Isolated single molecule is removed from a kink site and attached to the end of a five-member chain. (c) and (d) A single molecule is removed from a three-member chain and attached to the end of a two-member chain. The imaging parameters are −1 V, 50 pA.

from a −1.5 V sample bias) while the STM tip is positioned above the molecule's center. Upon pulsing, molecule 2 rotates counterclockwise by 60°. Molecule 1 was unaffected by the nearby voltage pulse to molecule 2. Figure 1(c) shows molecule 1 after it has been subjected to the same manipulation procedure, and subsequently has rotated. This manipulation process is completely reversible, as seen in Figs. 1(d) and 1(e), which show molecules 1 and 2 returned to their original states after the application of additional identical pulses. The switching success rate per tip voltage pulse depends on the detailed configuration of the STM tip apex. Different tips yielded success rates from 40% to near 100% under similar voltage pulsing conditions. For a given STM tip, the switching success rate did not depend sensitively on either the precise lateral tip position above the molecule or the tip voltage pulse width or amplitude. For most tips, the −3 V, 1 μs voltage pulse amplitude and width used above was found to be optimal within a parameter range of −6 to 7 V and 1 to 1000 μs.

In addition to rotating azobenzene molecules around anchor sites, we are also able to slide them laterally across the Au surface using the STM tip. This has been used to change the length of one-dimensional azobenzene chains. Figure 2 shows two demonstrations of this ability. In Fig. 2(a), a single azobenzene molecule residing at a kink site is pulled onto the end of a five-member azobenzene chain to create the six-member chain seen in Fig. 2(b). Figure 2(c) shows a single azobenzene molecule being detached from one short azobenzene chain and then being reattached to the end of a different small chain [Fig 2(d)]. The "sliding" technique[17] was employed to achieve both manipulations with typical moving parameters of 50 mV, 600 pA.

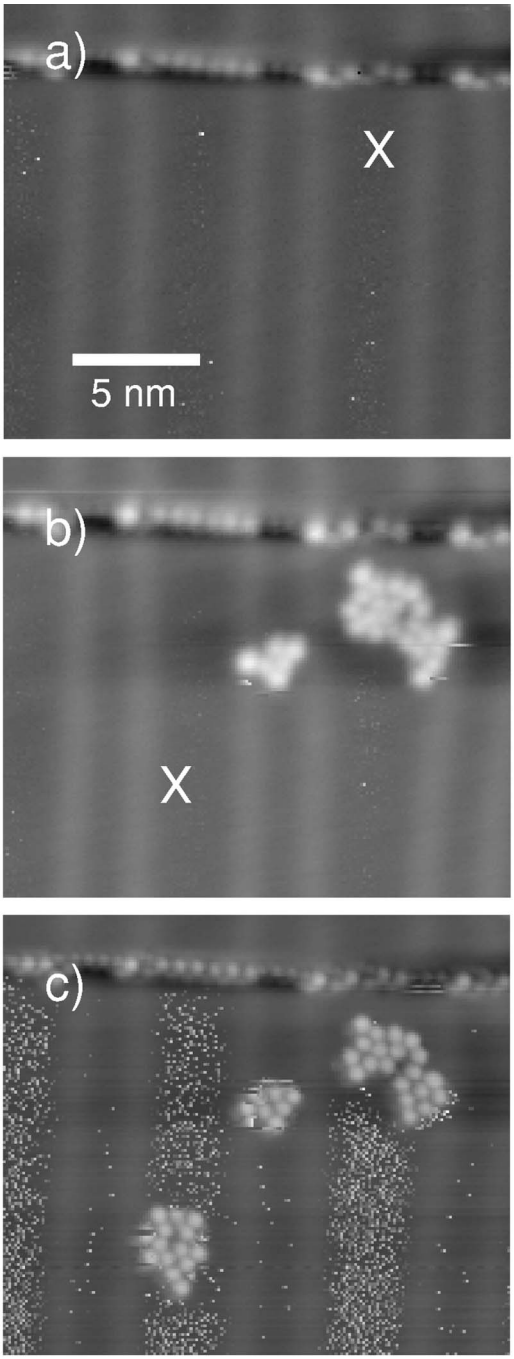

FIG. 3. The anchor-site creation manipulation at T=50 K. The tip voltage pulse (−6 V, 1 μs) at the position marked by "X" in (a) subsequently creates a region of stably adsorbed molecular clusters as seen in (b). A second pulse indicated by an "X" in (b) creates the additional cluster seen in (c). Differences in image quality are caused by slight tip changes during the manipulation process. The imaging parameters are −1 V, 50 pA.

Successful manipulation of azobenzene molecules via the sliding technique is hindered by the fact that azobenzene

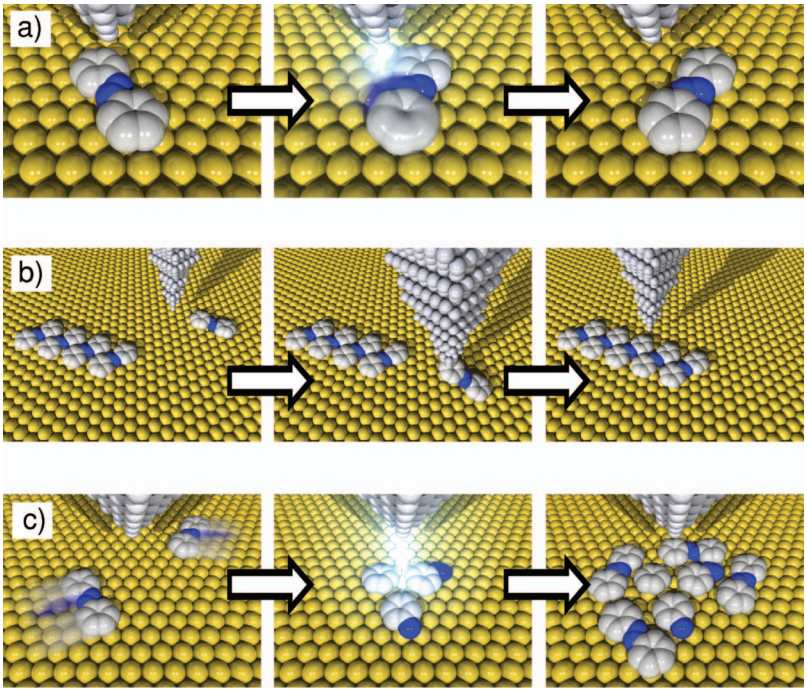

FIG. 4. (Color) Three sketches illustrating azobenzene manipulation techniques. (a) Bistable rotational switching: a single azobenzene molecule is induced by a tip voltage pulse to rotate clockwise by 60°. (b) Lateral translation: an isolated azobenzene molecule is bound to the STM tip and slid to join a four-member azobenzene chain. (c) Anchor-site creation: azobenzene molecules diffusing beneath the STM tip are damaged by a voltage pulse, causing them to bind to the surface and create a stable cluster.

adsorbates bind stably only to surface defects or molecular clusters at the temperature investigated (T=34 K). Events that cause the tip to lose contact with the molecule during manipulation thus free the molecule to instantly diffuse away from the tip torwards distant binding sites. We found that the most reliable technique for precisely positioning azobenzene molecules is to move the STM tip (with a captured azobenzene molecule) across fixed molecular chains from one side to the other [as indicated by the dashed lines in Figs. 2(a) and 2(c)], thereby allowing the chains to capture the manipulated molecule from the tip.

At higher sample temperatures (T>50 K), azobenzene molecules diffuse freely across the surface and do not bind singly at kink sites or even in the molecular chains of Fig. 2. Figure 3(a) shows an image of a Au(111) surface at T =50 K that has a coverage of azobenzene equal to the coverage seen in Fig. 2. However, the Au(111) terrace appears free of azobenzene molecules (although there is some step edge adsorption). Azobenzene molecules on the terrace diffuse too quickly to be observed by the STM tip, but appear as increased "flicker" noise in our images.

We find that it is possible to bind diffusing azobenzene molecules at this temperature to artificial anchor sites positioned on the Au(111) terraces. These anchor sites are created by applying voltage pulses to the STM tip. Figure 3(b) shows the results of applying a −6 V, 1 μs long pulse to the location marked "X" in the previously clean region of Fig. 3(a). Two immobilized clusters of azobenzene molecules are subsequently found in that region: a cluster of ten molecules at the precise location of the tip pulse and a smaller satellite cluster of three molecules. A second identical tip voltage pulse applied to the spot marked "X" in Fig. 3(b) creates a new cluster of seven molecules [seen in Fig. 3(c)]. The voltage pulsing parameters of −6 V, 1 μs used above were generally optimal for this manipulation category, although the threshold for manipulation was typically −4 V, 1 μs.

We now discuss possible physical mechanisms involved in the three azobenzene manipulation modes that we have observed. We begin with the bistable orientational switching. The bistable orientational states of single azobenzene molecules bound to kink sites are clearly influenced by the surface and molecular symmetries. As illustrated in the sketches of Fig. 4(a), the close-packed Au(111) surface atoms and the azobenzene phenyl rings both possess a quasi-sixfold symmetry. The herringbone kink defect breaks this symmetry and induces local minima in two of the six possible configurations. Voltage pulsing above a molecule either reduces the energy barrier between the two orientation configurations, allowing thermal activation between states, or it may directly provide enough energy to the molecule to excite it above the rotational barrier. The latter mechanism has been observed previously in single molecule systems such as acetylene on Cu(100),[12] and *cis*-2-butene on Pd(110).[13]

Our ability to laterally manipulate azobenzene is influenced by the fact that azobenzene molecules bond to each other only in specific configurations, most likely due to a modified hydrogen-bonding mechanism.[16,18] This causes laterally manipulated azobenzene molecules to "snap" precisely onto the ends of chains in perfect alignment [see Fig. 4(b) sketch]. Molecules cannot be stably positioned on a terrace in the absence of a defect or stationary molecular cluster because the azobenzene diffusion barrier is so low on Au(111) (even at a reduced temperature of T=34 K).

The third manipulation technique, anchor-site creation, is useful in this context because it allows the definition of positions on a metal terrace that can serve as the starting point of an artificial molecular nanostructure. The mechanism of anchor-site creation involves an irreversible change at the gold surface that creates a defect binding site. Because the gold surface near the anchor site appears undamaged, we believe that the creation of the anchor site is due to tip-induced damage to azobenzene molecules diffusing beneath

the tip during the voltage pulse. This proposed mechanism is sketched in Fig. 4(c). Here damaged azobenzene molecules bind to the surface beneath the tip, and provide a stationary point for other diffusing molecules to collect. Damage to molecules might include hydrogen atom dissociation or even phenyl ring opening or dissociation. Phenyl ring dissociation is suggested by the frequent observation of clusters made up of *odd* numbers of lobes. This technique is similar to other tip-induced lithography techniques that involve the cracking of a background gas in the junction region beneath the tip to deposit various substances.[19,20] The difference here is that in our case the reservoir of molecules is a 2D gas diffusing on the surface rather than a 3D gas diffusing through the vacuum chamber.

In conclusion, we show that azobenzene molecules can be manipulated in a number of ways on the Au(111) surface. Single azobenzene molecules adsorbed at herringbone kink sites are bistable and can be reversibly switched between two configurations. Lateral STM manipulation can be used to shuttle single molecules between anchor sites, allowing the construction of molecular structures. At higher temperatures, where azobenzene undergoes strong thermal diffusion, STM tip voltage pulses can be used to create new anchor sites for molecular clustering.

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