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Reorientation of a Single Bond within an Adsorbed Molecule by Tunneling Electrons

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ABSTRACT: Scanning tunneling microscopy offers the exciting possibility to manipulate individual molecules by vibrational excitation via inelastically tunneling electrons. The electrons transfer energy into molecular vibrational modes, leading to breakage or formation of individual bonds. It is challenging to precisely control intramolecular changes by this process. We demonstrate that for 4,4′-dihydroxyazobenzene adsorbed on Au(111) or Ag(111), the manipulation facilitates rotation of the OH end groups around the C−O bond between metastable states; this corresponds to a reorientation of the hydrogen, the ultimate limit of a conformational change within a molecule.

Scanning tunneling microscopy (STM) offers the exciting possibility to manipulate individual molecules by vibrational excitation via inelastically tunneling electrons (IET manipulation).[1] Molecular bonds[2] and bonds to the surface[3] can be broken by IET manipulation. More subtle changes to the molecules can result from conformational changes that are likewise induced by IET manipulation.[4−9] More recently, hydrogen bonds between molecules[10] have been rearranged and hydroxyl dimers have been induced to flip.[11] Other vibrationally induced changes of small lateral dimensions include charge switching on a single donor,[12] changing a Pt dimer among four configurations on Ge(001),[13] bending of a bond within a chloronitrobenzene molecule,[14] and changing the adsorption sites of Ag atoms on Ag(111)[15] or a CO_2 molecule bound to an oxygen atom on Ag(100).[16] The spatial limit of similarly small changes within molecules has not yet been reached. In this article, we present manipulation experiments on 4,4′-dihydroxyazobenzene adsorbed on Au(111) or Ag(111). We demonstrate that IET manipulation leads to changes in the appearance of parts of the molecule. These changes result from changes in the symmetry of the end groups with respect to the tunneling direction, indicating an induced rotation of the smallest part of the molecule around a single bond.

STM, scanning tunneling spectroscopy (STS), and IET manipulation measurements were performed with a low-temperature scanning tunneling microscope under ultrahigh vacuum (UHV) conditions. The Ag(111) and Au(111) surfaces were cleaned by repeated cycles of Ne^+ sputtering and annealing. 4,4′-Dihydroxyazobenzene was synthesized according to a published procedure[17] and sublimed under reduced pressure at 398 K to remove water. The molecules were deposited from a thoroughly outgassed Knudsen cell onto the surface at 213−233 K at a rate of (7.4 ± 0.5)% monolayer/min. After exposure, the sample was transferred to the microscope, which was operated at a temperature of 5 K. For STS and IET manipulation, the tip was positioned above the molecule and the feedback loop was switched off. For STS, the voltage was swept over the range of interest while a sinusoidal modulation voltage was superposed, and the signal was recorded using the lock-in technique. For IET manipulation, a voltage of a few volts was applied for microseconds to seconds. During the manipulation, the tunneling current was recorded, and a steplike change in the tunneling current indicated a successful manipulation. A subsequent STM image verified the result of the manipulation.

4,4′-Hydroxyazobenzene is a derivative of azobenzene ($H_5C_6N{=}NC_6H_5$) bearing hydroxyl groups at the two para positions (Figure 1a). The rotation barrier of the OH group around the C−O single bond is very low. Single molecules imaged on both Ag(111) and Au(111) exhibited a dumbbell shape (Figure 1b−d), consistent with those of other para-substituted azobenzene derivatives.[9] The distance between the two maxima is (0.7 ± 0.1) nm, which is between those found for native azobenzene and several derivatives.[9] It is considerably shorter than the total length of the trans isomer in the gas phase (1.3 nm) but slightly larger than the distance between the phenyl rings. This reflects the slight charge-pulling effect of the hydroxyl groups. The apparent height of our azobenzene derivative was 130 pm on Au(111) and 70 pm on Ag(111), both of which are in the typical range for azobenzene derivatives on metal surfaces.[9] Surprisingly, this apparent height was not the same for all of the adsorbed molecules on the same surface, even with the same tunneling parameters. The variation was particularly large within supramolecular structures (Figure 1e). The line scan (Figure 1f) showed a height variation of almost 40 pm.

Likewise, the molecules exhibited different apparent heights within differently ordered structures that formed on Ag(111) depending on the (local) coverage. At coverages below 1 molecule/nm^2, three or four molecules were connected at a knot and interacted via their end groups (Figure 2a). In the close-packed layer (1.7 molecule/nm^2), a herringbone-like pattern was observed (Figure 2b). While in the more open structures the difference in height did not seem to follow any specific pattern (Figures 1e and 2a), there was a distinct checkerboard-like pattern in the close-packed structure (Figure

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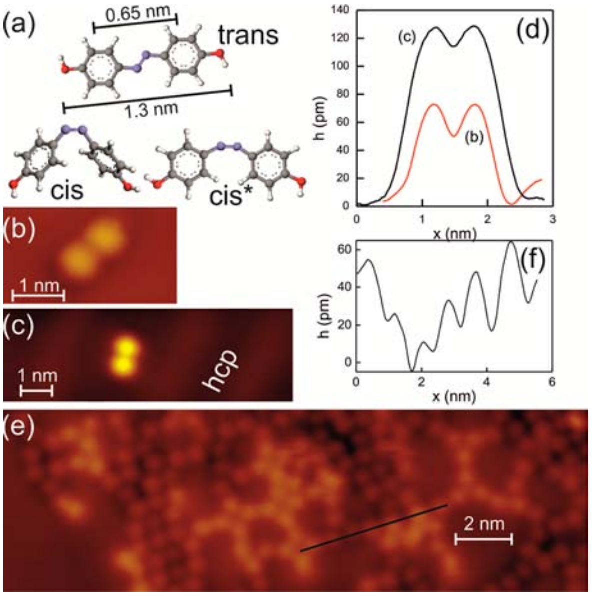

Figure 1. (a) Ball-and-stick models of 4,4′-dihydroxyazobenzene isomers: (top) trans isomer and (bottom left) cis isomer in the gas phase as calculated semiempirically using the Parametric Method 3 (PM3)-parametrized MNDO Hamiltonian;[18] (bottom right) surface-adapted cis* isomer, as observed for other azobenzene derivatives.[9] In the cis* isomer, both phenyl rings are parallel to the surface at the expense of an increase in the N═N−C angle compared with the three-dimensional cis isomer.[5] (b, c) STM images of single molecules adsorbed on (b) Ag(111) (360 pA, 299 mV) and (c) the fcc domain of Au(111) (15 pA, 59 mV). In (c), faint lines are domain boundaries, and an hcp domain is marked. (d) Line scans along molecular axis and across the maxima in (b) and (c). (e) STM image of supramolecular structures on Ag(111) (160 pA, 210 mV). (f) Scan along the black line in (e).

2b,c) with four different apparent heights between ∼45 and ∼80 pm.

We were able not only to record these different apparent heights but also to change them selectively for an individual protrusion of one molecule within such a supramolecular structure (Figure 3). Figure 3a shows a double row of molecules on Ag(111) with a single molecule attached at the end of the lower row. The right-hand protrusion of the last molecule within the double row, to which the single molecule is attached, shows a larger apparent height than its other protrusion. In the molecule directly above this one, the right-hand protrusion shows a smaller apparent height (Figure 3c, black line). After manipulation, the single molecule was attached to the upper row. This change in binding was accompanied by a reversal of the apparent heights of the protrusions marked by the arrows in Figure 3a,b by more than 10 pm (Figure 3c, red line). In contrast, the apparent height of the turning molecule did not change within the experimental accuracy (Figure 3d,e).

What could be at the origin of this striking difference in apparent height? On the basis of the imaging properties of molecules by STM, either the molecules themselves differ or the same molecules are in different binding configurations. In the former case, different conformers,[19] different isomers,[20] or different molecules as a result of dehydrogenation[21] are possible options. In the latter case, different adsorption sites,[22] or different bindings to other molecules are possible origins. In the

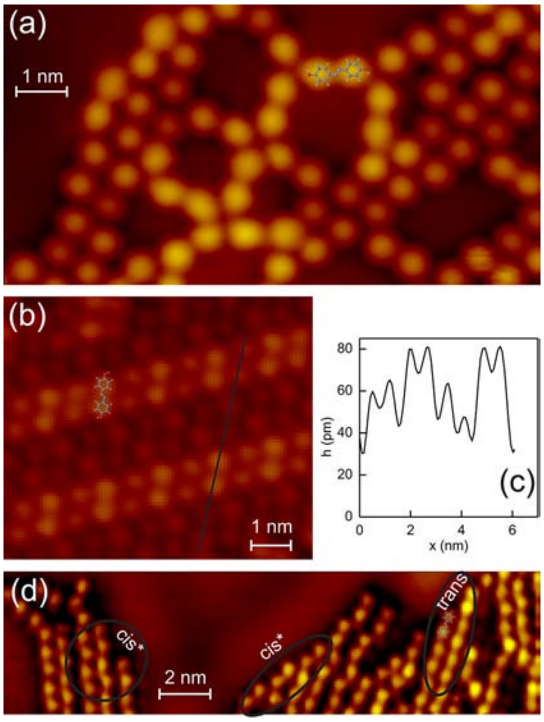

Figure 2. (a, b) STM images of supramolecular structures of 4,4′-dihydroxyazobenzene on Ag(111): (a) open structure at a low local coverage of <1 molecule/nm^2 (51 pA, 125 mV); (b) close-packed structure at a high coverage of 1.7 molecules/nm^2 (100 pA, 219 mV). In each image, one molecule each is marked using a ball-and-stick model. (c) Scan along the black line in (b), normalized to the surface value outside of the region shown. (d) STM image recorded using a modified tip (59 pA, 125 mV). Some slightly bent cis* isomers and straight trans isomers are circled.

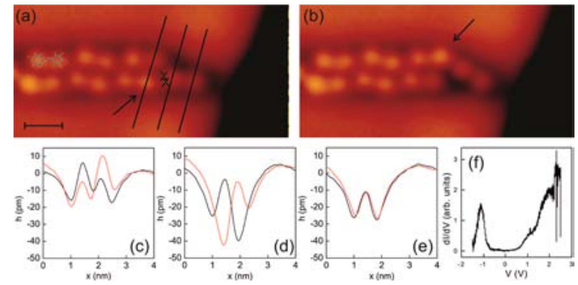

Figure 3. (a, b) STM images (97 pA, 137 mV) showing IET manipulation (2 V, 9.5 nA for 0.2 s with the tip at upper cross at the beginning of manipulation and at lower cross at the end of manipulation) of 4,4′-dihydroxyazobenzene within a superstructure on Ag(111): (a) before manipulation; (b) after manipulation. Arrows point to the protrusions whose apparent heights were changed by the manipulation. In (a), one molecule is superimposed with a ball-and-stick model. (c−e) Scans along the (a) left, (b) middle, and (c) right black lines in (a): black curves, before manipulation; red curves, after manipulation. (f) STS spectrum with f_{mod} = 823 Hz and V_{mod} = 6 mV.

following we present experimental evidence that rules out all but two of these possibilities.

First, it is unlikely that the different apparent heights result from different isomers. To date, only the three types of isomers depicted in Figure 1a have been deduced for a variety of adsorbed azobenzene derivatives:[9] the planar trans isomer adsorbed parallel to the surface; the three-dimensional cis isomer, which produces a single protrusion in STM images, as observed for native azobenzene on Au(111);[20] and the surface-adapted cis* isomer induced by additional covalent-type binding of the end groups,[20] which was found for 4-amino-4′-nitroazobenzene on Au(111).[5] This number of isomers is not consistent with the observed number of different apparent heights. Visualization of the isomers with a tip modified by molecule adsorption corroborated this interpretation (Figure 2d). This tip resolved more clearly the region of the azo group. In all cases, pairs of protrusions showed a connecting region, and single protrusions indicative of the cis isomer were not observed. Thus, 4,4′-dihydroxyazobenzene adopts either the trans form or the cis* form. For some of the molecules, the modified tip imaged a connection in line with the two protrusions, indicative of the trans isomer; for others, the connection was slightly off line, indicative of the cis* isomer.[5] However, the difference in apparent height was not correlated with the two isomers. Instead, the height varied for both isomers and for individual protrusions of a molecule (Figure 2d).

We next used IET manipulation to rule out further possibilities. On Au(111), the molecules could be rotated and diffused at a manipulation voltage of ∼1.5 V (Figure 4a−d).

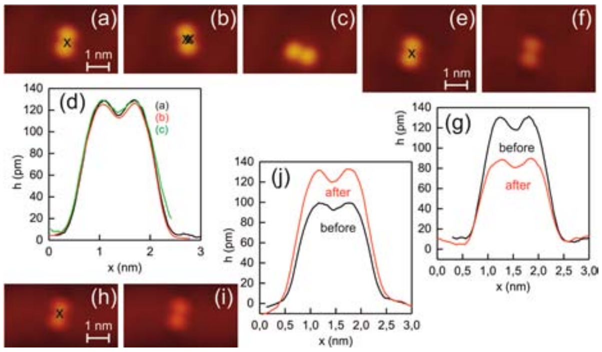

Figure 4. (a−c) STM images showing rotation and diffusion induced by IET manipulation (−1.5 V, 0.18 nA for 479 ms) of single 4,4′-dihydroxyazobenzene molecules on Au(111): (a) before manipulation; (b) after the first manipulation and before the second manipulation; (c) after the second manipulation. (d) Line scans for (a−c). (e, f) STM images showing the reduction in apparent height upon IET manipulation (3.5 V, 1.8 nA for 24 ms): (e) before manipulation; (f) after manipulation. (g) Line scans for (e) and (f). (h, i) STM images showing the increase in apparent height upon IET manipulation (−0.5 V, 0.23 nA for 21.84 ms): (h) before manipulation; (i) after manipulation. (j) Line scans for (h) and (i). All of the STM images were recorded at 15 pA, 59 mV; crosses show the tip locations for manipulation; all of the line scans were along the long axis of the molecule and across the two maxima.

Figure 4a shows a single molecule adsorbed on a face-centered cubic (fcc) domain of Au(111). Upon IET, the molecule rotated by 23°. As the rotation was around a point outside of the molecule, we observed a combination of rotation with diffusion. This was even more obvious in the second manipulation. The molecule was rotated by 80°, and the center of mass was displaced by approximately 0.5 nm. Though the sixfold symmetry of the surface excluded the possibility that the molecule had the same adsorption site in all cases, the apparent height of the molecule changed by less than 4 pm. This and many other manipulations with the same results showed that a difference in adsorption site is not at the origin of the apparent height change of tens of picometers.

Though the experiment presented in Figure 3 as well as the STM images in Figure 2 suggested that the apparent height difference involved binding, we showed next that the apparent height change was also possible for single molecules. To do this, we manipulated the same molecule with a higher voltage of −2.5 V (Figure 4e−g). This manipulation led to neither diffusion nor rotation. Instead, the apparent height of the molecule was reduced from ∼130 pm to below 90 pm. Thus, changes in binding could not be the sole origin of the apparent height change. Another manipulation of the same molecule with negative polarity restored the original apparent height (Figure 4h−j). The reversibility shown in Figure 4e−j excludes dissociation of an atom (e.g., H) from the molecule as the origin of the apparent height change.

Putting all of these results together, we conclude that conformational changes were responsible for the apparent height differences. For single molecules, only two different apparent heights are possible, but at least four different apparent heights were observed within supramolecular structures. Thus, the surface stabilizes two conformers and binding stabilizes additional ones. Two conformational changes apart from isomerization could be envisioned for 4,4′-dihydroxyazobenzene: rotation of the phenyl ring around the C−N bond[8] and rotation of the OH group around the C−O bond. The dependence of the number of conformers on the presence of binding partners suggested the latter, as a hydrogen bond to another molecule cannot stabilize a nonparallel adsorption of the phenyl ring.

Our interpretation of a conformational change was corroborated by the experiments shown in Figure 5, which demonstrated that we could change the orientation of the two OH groups selectively. Manipulation at 2.5 V reduced the apparent height of the upper protrusion in Figure 5a,b. In the other manipulation series (Figure 5d−f), the first manipulation (d to e) reduced the height of the lower protrusion from above 120 pm to below 100 pm, and the second protrusion's height was reduced to a similar value in a second manipulation step (e to f). This selective change also supports our interpretation of a conformational change.

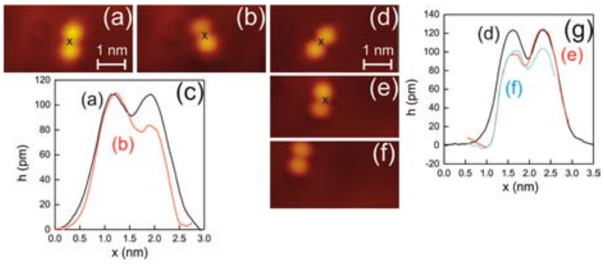

Figure 5. IET manipulation of 4,4′-dihydroxyazobenzene on Au(111). (a, b) STM images (a) before and (b) after manipulation at 2.5 V and 4 nA for 8 ms. (c) Line scans for (a) and (b). (d−f) STM images (d) before the first manipulation at 3 V and 0.75 nA for 1.4 s, (e) after the first manipulation and before the second manipulation at 2.6 V and 1.2 nA for 1.11 s, and (f) after the second manipulation. (g) Line scans for (d−f). STM images were recorded at 59 mV and (a, b) 15 or (d−f) 10 pA; crosses show the tip locations for manipulation; all of the line scans were along the long axis of the molecule and across the two maxima.

For 4,4′-dihydroxyazobenzene on Ag(111), the thresholds for the apparent height changes were found to be −2 V and below and +1.5 V and above, although the yields at the thresholds were very low ($2.4 \times 10^{-11}/e^-$ at −2 V and $4.2 \times 10^{-11}/e^-$ at +2 V). A 15-fold increase in yield was observed at +3 V. The IET manipulation could be initiated either by direct vibrational excitation of the molecule, by the electric field between the tip and the sample, or by transient occupation of an electronic orbital. The threshold at some voltage excludes the possibility that the change is induced by direct vibrational excitation. Furthermore, we changed the field via different manipulation set points over a range corresponds to a change in current by a factor of 250. The independence of the yield per electron during this change excludes field-induced manipulation. These experiments therefore point to a process that involves the transient occupation of a molecular orbital by an electron. The STS spectrum in Figure 3f provides evidence that there are molecular orbitals in the voltage range of manipulation. The range of the spectrum was limited by induced processes to the molecule, and thus, a direct assignment to a specific orbital is not possible here. However, the spectrum shows that the process cannot be induced by occupation of the frontier orbitals (HOMO and LUMO) but only by occupation of higher- or lower-lying orbitals, as in the case of cis–trans isomerization of 4-anilino-4′-nitroazobenzene.[23]

In conclusion, we have demonstrated that STM allows manipulation of the internal structure of a molecule between stable conformers that differ only in the orientation of a single bond. Such small changes offer unprecedented possibilities. For instance, it could be utilized to arrange molecules in different specific orientations prior to initiating their reactions in order to obtain different products. This should be possible for a variety of different molecules with properly designed end groups

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Notes

The authors declare no competing financial interest.

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