

Molecular switches: Isomerization of single azobenzene derivatives

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Introduction

The investigation of single molecules has become an important and well-established research field in the last years, driven by the prospect for fundamental electronic and mechanical device miniaturization [1]. Understanding and controlling conformational changes of single molecules is very important in this regard. For this purpose, the scanning tunneling microscope (STM) at low temperature constitutes a powerful tool, as it not only allows precise sub-molecular imaging of single molecules but also permits the manipulation of atoms and molecules [2]. Recent experiments show that conformational changes within a molecule can be mechanically induced by the STM tip [3]. Molecular rotation [4, 5] and vibration [6] can be achieved by electronically exciting molecules with tunneling electrons, while diffusion [7] or desorption [8] of molecules adsorbed on surfaces are also induced by the intense electric field present between the STM tip and the sample surface. Such a field is strongly inhomogeneous and in the range of 0.2-2 V/Å, concentrated in the vicinity of the tip (i.e. in a radius of a few hundred Angstrom) [2]. Its strength can reach values required for field ionization and the desorption of an atom.

Looking for molecules suitable for application in molecular electronics, the current research interest is focusing on molecular switches [9, 10]. A molecular switch undergoes a reversible transformation between at least two distinct stable switching states, usually geometrical or valence isomers, associated with different physicochemical properties based on a change in molecular geometry and/or electronic distribution [9]. By using a Cu TBPP molecule, it has been shown how the tip of a scanning tunneling microscope can be used to trigger the switching mechanism of a single molecule [3]. Here, the interatomic forces between tip and molecule have been used for the manipulation, i.e. to rotate a single molecular leg. In this way, different conformations with characteristic junction resistances have been created in a controlled way.

The azobenzene molecule represents a very interesting example of such a molecular switch and its operating mechanism based on a trans-cis isomerization of a double

bond is conceptually related to the basic principle of vision in the human eye. In the electronic ground state, azobenzene adopts two different conformations: a nearly planar trans and a non-planar, three-dimensional cis form [11]. The reversible switching between these two isomers is well investigated in solution and in the gas phase whereby the ground state barrier for isomerization is typically overcome by photo-excitation [12-15].

Results

The aim of the presented work is to study the possibility of using azobenzene derivatives as molecular switches, i.e. to isomerize single molecules on a metal surface in a controlled way [16]. **Figure 1a** shows the investigated molecule: 3,3',5,5'-tetra-tert-butyl-azobenzene, called TBA. It consists of an azobenzene core and four lateral tert-butyl groups that should increase the separation between surface and the azobenzene π -system, leading to increased surface mobility and potentially lower electronic coupling. On the other hand, the substituents do not significantly alter the electronics of the azobenzene chromophore and do not impart steric hindrance upon the isomerization process. By means of the molecular appearance in STM images, it is important to note that the four symmetrically placed legs facilitate conformational analysis, because they appear as intense lobes and thus act as markers. The molecules were synthesized by oxidative dimerization of 3,5-di-tert-butyl-aniline and exhibit the photochemical and thermal isomerization behavior typical for azobenze-

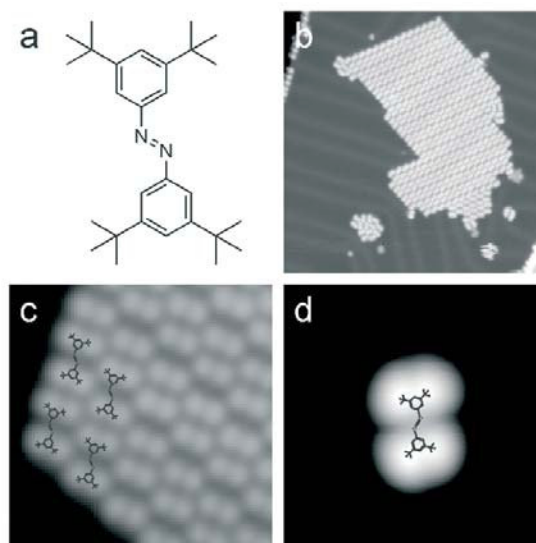


Figure 1: (a) TBA molecule. (b) STM image ($40 \times 40 \text{ nm}^2$) of a molecular island on Au(111). The exact adsorption configuration of the molecules can be determined from the corner of an island in an enlarged STM image (c), the molecular structure is indicated. (d) shows the STM image of a single TBA molecule.

ne derivatives in solution [16].

The experiments were performed under ultrahigh vacuum conditions (base pressure of 10^{-10} mbar) at a temperature of 5 K using a homebuilt STM, described in detail elsewhere [17]. The Au(111) substrate was prepared by several cycles of sputtering with Ne ions and subsequent annealing at 800 K. The molecules were deposited by evaporation from a homebuilt Knudsen cell kept at 370 K, and the dosage was monitored via a quartz crystal micro-

balance. During the deposition of the molecules, the sample was kept at room temperature. All images are recorded in constant current mode with a tunneling current of 0.1 nA and a bias voltage of 1 V on the sample.

An overview STM image of TBA molecules on Au(111) after deposition is shown in **Figure 1b (Page 22)**. The molecules are mobile after adsorption, as they cover step edges and form islands, but are also found isolated on terraces. Islands formed by less than about 40 molecules are disordered, i.e. the molecules are not equally oriented. As the number of molecules increases, the intermolecular interaction leads to the formation of highly ordered islands. The position and orientation of individual molecules inside these islands is shown in **Figure 1c (Page 22)**: The molecules form parallel rows indenting with each other. Isolated molecules (**Figure 1, Page 22**) are always positioned at the elbows of the Au(111) herringbone reconstruction. Even though the molecule itself is not chiral, the molecule-surface system is chiral [18], which becomes clear in the case of a single molecule (d) with a rather rhombic and not a rectangular shape.

Each molecule appears as four lobes with an apparent height of 2.7 ± 0.1 Å arranged in a rhombic shape. According to the dimensions of the molecule in the gas phase, the lobes can be assigned to the tert-butyl groups while the central azobenzene part is not visible. All observed molecules are in the same planar configuration that we assign to the trans isomer (**Figure 1a, Page 22**), which is known to be the energetically favored configuration in the gas phase [11]. The complete missing of cis isomers on the surface is expected, because any heating process (for deposition) increases the fraction of the trans isomers on the expense of the cis molecules [11,13].

We have investigated the isomerization process in the ordered molecular islands, where a large number of molecules is present. To induce the isomerization, we have applied voltage pulses of 2 V with the STM tip positioned above an island. After these pulses, many molecules have changed appearance, showing a larger height of 4.1 ± 0.3 Å. These bright molecules are stable and to let them precisely restore their initial appearance we have to apply a further pulse, as shown in **Figure 2**. As one can see in **Figure 2a**, the isomerization process has no consequence on the neighboring trans molecules, which remain unchanged. The cis form appears with a bright central intensity maximum, while three lateral lobes in an approximately triangular shape can be resolved, completely different from the planar trans conformation. This shows that, in contrast to the trans isomer, the cis isomer is not planar, in agreement with the molecular conformation in the gas phase [11] and as observed by STM [19] for azobenzene molecules on Au(111).

Such switching experiments can be reproduced several hundred times allowing us to conclude that the observed changes are due to the isomerization of single molecules from the trans form to the cis form, and back to the trans form [16]. The reversibility of the experiment and its high reproducibility exclude molecular dissociation or the presence of any contamination as cause for the observed change of the molecular appearance. The switching of an isolated molecule is very rare because, under the effect of

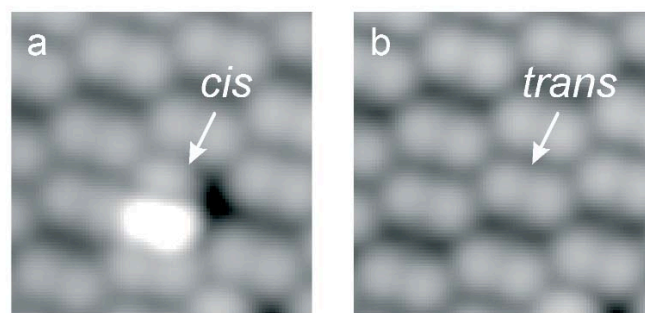


Figure 2: Isomerization process from cis to trans. (a) and (b) show STM images (both $3.5 \text{ nm} \times 3.5 \text{ nm}$) before and after the isomerization. The bright molecule in (a) is in the cis state and exactly returns to the trans state in (b), where all visible molecules are trans isomers, after applying a voltage pulse.

a voltage pulse, the molecule can move or rotate thereby efficiently competing with the isomerization process. This effect is avoided in the islands when the molecules are stabilized by each other.

In order to understand the driving mechanism for this isomerization process, we have studied the dependence of the bias voltage, required for the isomerization, on the tip height (**Figure 3**) [16].

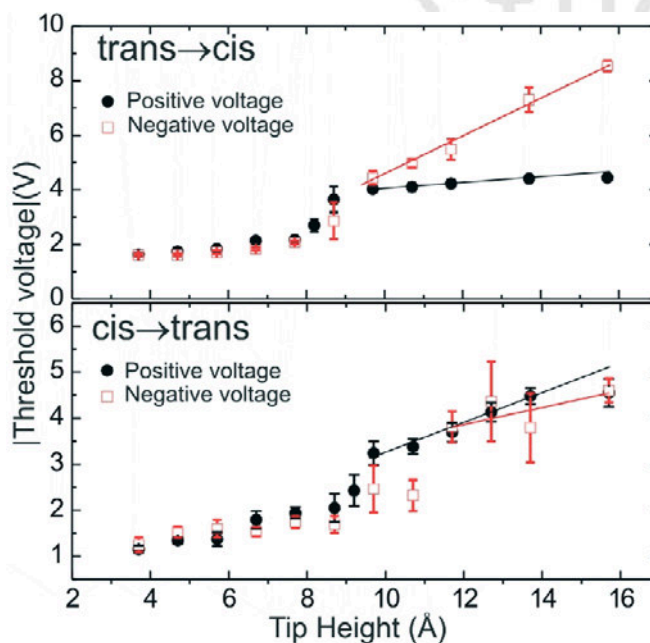


Figure 3: Plot of the threshold voltage as a function of tip height for the trans \rightarrow cis isomerization (top) and for the cis \rightarrow trans isomerization (bottom) for positive (electric field points towards the STM tip) and negative voltage polarities. Reprinted from Ref. 16. Copyright 2006 American Chemical Society

The experimental points have been measured by fixing the tip at a specific height, referred to the bare Au(111) surface, and applying a voltage pulse for a fixed time $t=30$ s. Starting from $V=0$, we increased the voltage by increments of 0.1 V until we observed a switching event in a lateral area of 80×80 Å from the tip position. Each sequence was repeated 10 times. The data show that switching is possible with positive and negative voltage polarities and the threshold voltage is not a constant value, characteristic in the case of electron resonant tunneling [5], but clearly increases (at tip heights >9.5 Å)

when retracting the tip. The isomerization process occurs also at very large tip distances where no tunneling current is flowing (the tunneling current decreases exponentially with the tip-surface distance). Even in the extreme case when the tip is 36 Å above the surface, we were able to switch molecules from trans to cis (after applying a voltage pulse of 6.8 V)! These results lead to the conclusion that the isomerization of TBA molecules on Au(111) is driven by the electric field in the STM junction, which does not involve the tunneling of electrons. Very recent theoretical calculations of P. Saalfrank et al. [20] for TBA molecules explain this mechanism: the electric field in the STM junction deforms the potential barrier of the molecule in the ground state thereby facilitating the switching process.

The approximately linear dependence of the threshold as a function of the tip height in **Figure 3 (Page 23)**, considering the large tip height regime (points above 9.5 Å), allows to quantize the required electric field. We find values of 0.1 V/Å and 0.7 V/Å for the trans → cis isomerization, while for the cis → trans it amounts to 0.3 V/Å and 0.4 V/Å. Points below 9.5 Å are not included in the plot because in this region there is a change in slope, probably related to electronic effects that come into play at small tip heights (i.e. large currents). These experimental values of the electric field are smaller than the calculated ones (about 1-2 V/Å) [20], which is likely due to the presence of the surface that enhances the permanent dipole and the polarizability of the molecule. It is important to mention the different slopes for positive and negative voltages in the case of trans → cis isomerization as compared to the cis → trans process (where the behaviour is very similar for the two polarities). These differences are presumably caused by the characteristic polarizability of the molecule and the orientation of its intrinsic dipole moment for the trans and cis configuration and intermediate configurations during the reaction.

Conclusions

We have shown that the isomerization of single azobenzene derivatives can be induced by using a scanning tunneling microscope. Isomerized molecules in the cis state appear brighter within the molecular islands due to their non-planar structure, in accordance with the configuration in the gas phase. The isomerization process is reversible as cis isomers precisely restore the trans configuration after a second voltage pulse. The dependence of this switching process on the experimental parameters shows for the first time that the process can be induced by the electric field in the STM junction and is thus possible without any electric current.

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STM imaging of molecules on a thin insulating film

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Introduction

Until recently, STM was the only technique allowing to image individual molecules adsorbed on surfaces. For this reason, single molecule studies were restricted to conducting substrates. Some strategies were developed to allow well defined electrical connexions to single molecules on metals, based on the synthesis of specially designed molecules [1], but these approaches are not suited for further developments, such as planar electrical connexions to a single molecule. The emergence and progress of AFM in the non-contact mode make now possible to image a single molecule on an insulating substrate [2], but this technique is rather difficult and molecular manipulations are not yet well mastered, as for STM. It was realized recently [3-6] that it is possible to use STM to study molecules adsorbed on ultrathin insulating films on conducting substrates. In this situation the insulating film decouples the molecule from the substrate, while still allowing the transport of a weak tunneling current through the structure. These studies constitute an intermediate step which is currently explored in PicoInside (<http://www.picoinside.org>)