Adsorption and Switching Properties of Azobenzene Derivatives on Different Noble Metal Surfaces: Au(111), Cu(111), and Au(100)

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The adsorption and switching behavior of 3,3′,5,5′-tetra-*tert*-butylazobenzene (*meta*-TBA) are investigated by low-temperature scanning tunneling microscopy on three different metal substrates: Au(111), Cu(111), and Au(100). The trans state is the most stable configuration after adsorption, displaying similar appearances in the STM images, independent of the substrate. However, the self-assembly and switching behavior is highly dependent on the chemistry and corrugation of the surface. On the Au(111) surface, the tip-induced isomerization is probed successfully and different driving mechanisms are characterized. The experimental images are in good agreement with calculated ones. However, the switching effect is completely suppressed on Cu(111) and Au(100).

Introduction

The development of electronic devices made of single or few functionalized molecules (molecular electronics) offers great potential in terms of device miniaturization, cost, and efficiency.[1] In order to fabricate such electronic components at the nanoscale level, single molecules should act as functional components such as rectifiers,[2] amplifiers,[3] or switches.[4] A molecular switch requires at least two stable switching states with different physical/chemical properties,[5] for instance a change in conductance.[6]

The azobenzene molecule represents a very interesting example of a molecular switch.[7] Its mechanism, based on a trans−cis isomerization, should lead to different conductance states when the molecule is positioned between two electrodes as proposed by theoretical calculations.[8] The reversible switching between the nearly planar trans isomer to the three-dimensional cis isomer is investigated in the gas phase and in solution and occurs by overcoming the ground-state energy potential barrier via photoexcitation followed by either $N{=}N$ bond rotation or N inversion.[9–13] In addition, there has been an electrochemical study in solution showing that the azobenzene radical anion, generated by electron transfer at the electrode surface, is able to undergo cis → trans isomerization only, not trans → cis isomerization.[14]

The scanning tunneling microscope (STM) at low temperature (LT) is a powerful tool for investigating and triggering functional molecules on surfaces at the atomic scale.[1] Low-temperature

STM studies of the adsorption of single azobenzene molecules at surfaces have been reported,[15–17] and very recent experiments have shown the reversible isomerization of the azobenzene molecule and derivatives via either tip-induced[18–20] or light-induced processes.[21,22]

All successful switching experiments so far were performed exclusively on Au(111) as the supporting substrate. Thus, as a further step in the detailed understanding of the isomerization process on surfaces, it is important to study the influence of the molecule−substrate interaction on the switching process. In this article, we present a comparative study of the 3,3′,5,5′-tetra-*tert*-butylazobenzene (*meta*-TBA) molecule on three different noble metal surfaces: Au(111), Cu(111), and Au(100). This molecule is a promising candidate for such a study because its isomerization on the Au(111) surface has already been demonstrated by using the STM tip[20] and UV light.[21,22] Note that, historically, the successful use of the Au(111) surface was proceeded by the attempts to utilize the Cu(111) surface detailed herein.

Experimental Methods

The synthesis of the *trans-meta*-TBA molecules has been described previously.[20] The *trans-meta*-TBA molecule carries four lateral *tert*-butyl groups (Figure 1a), which act as spacers for decreasing the electronic coupling between the molecule and substrate without affecting the electronic properties of the azobenzene core. The latter was verified by the close resemblance of the obtained UV/vis absorption spectra of *trans-meta*-TBA in nonpolar cyclohexane solution displaying an absorption maximum $\lambda_{max} = 322$ nm ($\varepsilon = 21500$ M^{-1}·cm^{-1}) close to that of the parent unsubstituted *trans*-azobenzene ($\lambda_{max} = 317$ nm) in the same solvent. The photochemical and thermal isomerization behavior[20] was monitored by UV/vis absorption spectroscopy and is reminiscent of azobenzene itself.[9,10] While irradiation of *trans*-TBA in cyclohexane solution using a 1000 W medium-pressure xenon lamp (XBO) equipped with an optical filter ($\lambda_{max\ T} = 357$ nm @ 35% T, fwhm = 43 nm) resulted in trans → cis isomerization yielding a cis/trans ratio

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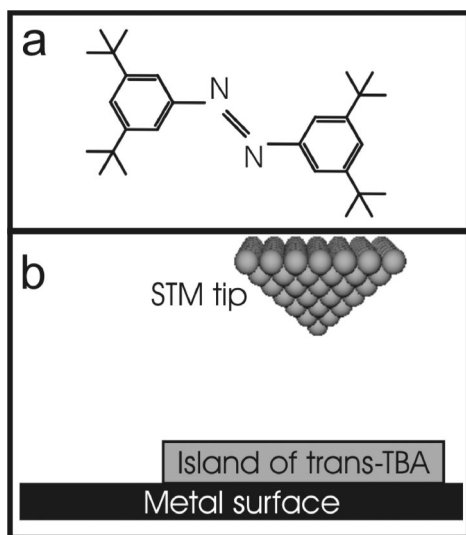⊥ CEMES-CNRS.
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Figure 1. (a) Chemical structure of *trans*-3,3′,5,5′-tetra-*tert*-butyl-azobenzene (*meta*-TBA). (b) Schematic of a switching experiment: The STM tip is positioned above an isolated molecule or a molecular island, and a voltage pulse is applied.

= 88.6:11.4 (photostationary state), the reverse cis → trans isomerization was induced either photochemically by using an appropriate optical cutoff filter ($\lambda_T > 400$ nm) or thermally at elevated temperatures (323 K).

The experiments were performed under ultrahigh vacuum conditions at a temperature between 5 and 7 K using a home-built STM.[23] Gold and copper surfaces were prepared by several cycles of sputtering with Ne ions and annealing at 800 and 770 K, respectively. The *trans-meta*-TBA molecules were deposited by evaporation from a Knudsen cell at about 370 K, and the dosage (in the submonolayer regime) was monitored via a quartz crystal microbalance. During the deposition of the molecules, the samples were kept at room temperature. After preparation, the samples were inserted into the LT-STM. All images were recorded in the constant-current mode applying the given bias voltage to the sample.

A scheme of the isomerization experiments in this work is shown in Figure 1b. They are all performed by positioning the STM tip at a fixed height above a molecular island with the feedback loop switched off and applying a voltage V_m (between 0 and 3 V) to the sample for a time between 0.1 and several 100 s. While applying these voltage pulses, the tunneling current versus time was recorded. The lower current limit, which we were able to measure, was 1 pA.

Results And Discussion

Au(111). After adsorption of *meta*-TBA molecules on Au(111), the molecules are mobile as they cover step edges and form islands but are also found isolated on terraces (Figure 2a). All molecules have the same appearance, that is, four protrusions, corresponding to the trans configuration (see below). Islands formed by less than approximately 40 molecules are disordered; that is, the molecules are not oriented equally (Figure 2b). As the number of molecules increases, the intermolecular interaction becomes dominant and leads to the formation of highly ordered islands (Figure 2a). The position and orientation of individual molecules inside ordered islands has been discerned from island corners as shown in Figure 2c. The molecules, indenting with each other, form parallel rows running at $\pm(5 \pm 3)°$ with respect to the close-packed directions of Au(111). The long axis of the molecules is oriented along one

of the close-packed directions of the substrate and neighboring molecules are aligned with each other. Notice in Figure 2a that the herringbone reconstruction underneath the island is still visible, indicating that the adsorbed molecules do not modify the covered Au(111) surface, which occurs in the case of a strong molecule−substrate interaction.[24]

Isolated molecules nucleate preferentially at the elbows of the herringbone reconstruction. In Figure 3a, an STM image of such a molecule on Au(111) is shown. The isolated molecule in the trans configuration 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 hardly visible.

The semiempirical atom superposition and electronic delocalization molecular orbital (ASED-MO) approach completed with a description of van der Waals forces (ASED+)[25] was used to obtain the conformation of the *meta*-TBA molecule. The structure of a *meta*-TBA molecule in the trans state, the most stable configuration, is presented in Figure 3c. The planar adsorption of the phenyl rings corresponds to a physisorption structure in which the *tert*-butyl-groups efficiently inhibit the mixing of the azobenzene's π orbitals with the substrate. By using the elastic scattering quantum chemistry (ESQC) calculation technique,[26] we have calculated the STM images. Figure 3b shows the calculated STM image of the *meta*-TBA molecule in the trans state. In good agreement with the experimental findings, the four *tert*-butyl groups give the dominant contribution to the image, while the central azobenzene part is hardly visible. From the comparison between experimental data and calculations, we conclude that after adsorption on Au(111) all observed molecules are in the planar configuration that corresponds to the trans isomer (see Figure 1a).

The *trans-meta*-TBA molecules can be isomerized to the corresponding cis state in a controlled way by using the STM tip[20] or by UV light.[21,22] In Figure 3d, such a cis isomer in a molecular island, imaged after a switching pulse with the STM tip, is shown in detail. It appears with a bright central intensity maximum (4.1 ± 0.3 Å), while three lateral lobes in an approximately triangular shape can be resolved. The STM images reveal that the cis state is markedly different from the planar trans state because it adopts a three-dimensional conformation. This appearance is in very good agreement with the calculated STM image of a *meta*-TBA molecule in the cis state, shown in Figure 3e. In the cis isomer, one phenyl moiety remains on the surface (in a similar geometry as in the trans conformation), where the two *tert*-butyl groups cause two lobes in the STM image (top of Figure 3d and e). However, in strong contrast to the planar trans isomer, the central azo (N=N) linkage of the molecule together with the second phenyl ring are oriented upward in the cis state. Although one *tert*-butyl leg at the surface gives rise to a weak lobe in the STM image (bottom of Figure 3d and e), the distinct central intensity maximum in the STM image corresponds to the *tert*-butyl leg pointing upward (see Figure 3f). The agreement between calculations and experiments indicates that the structure of the cis isomer is not strongly modified by the presence of the other molecules in the islands. In fact, the calculated image corresponds to an isolated cis isomer, whereas cis isomers in the experiments are adsorbed in islands.

By studying the dependence of the bias voltage, required for isomerization, on the tip height, we have shown recently[20] that at large tip heights (≥ about 10 Å) the switching process is driven by the electric field in the STM junction and does not
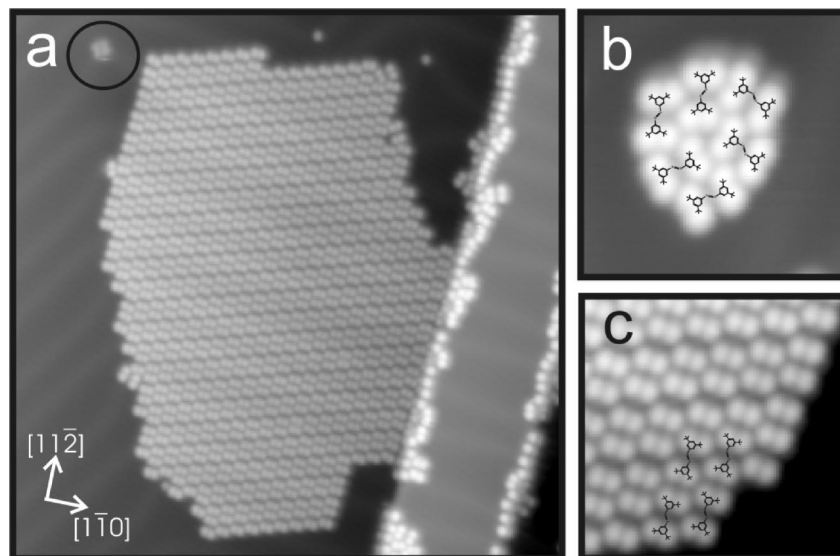
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Figure 2. (a) Overview STM image (390 × 390 Å^2) of *meta*-TBA adsorption on Au(111). A large ordered island of molecules and two surface steps covered by molecules (right) are visible. An isolated molecule is found at the elbows of the Au(111) reconstruction (indicated by a circle). (b) STM image of a molecular island made of six differently oriented molecules. The size of the image is 65 × 65 Å^2. (c) Corner of a molecular island (70 × 70 Å^2), which allows us to extract the molecular island structure, as indicated in the image. Note that the choice of the molecular chirality for the superimposed molecular models is arbitrary. In all images, the STM parameters are $U = 1$ V, $I = 0.1$ nA, and $T = 5$ K.
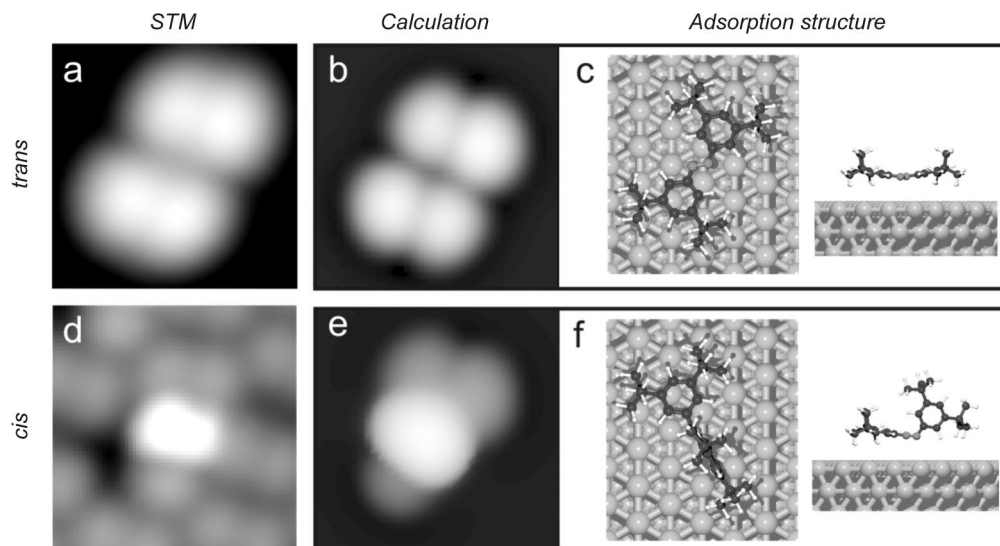

Figure 3. (a) STM image (24 × 24 Å^2) of a *meta*-TBA molecule in the trans form on Au(111). The STM parameters are $U = 1.3$ V, $I = 0.05$ nA, and $T = 5$ K. (b) Calculated STM image of *meta*-TBA molecule in the trans form on Au(111). (c) Adsorption structure corresponding to the calculated STM image of the trans isomer in part b in a front view (left) and in a side view (right). (d) STM image (24 × 24 Å^2) of a *meta*-TBA molecule in the cis form. The STM parameters are $U = 1$ V, $I = 0.1$ nA, and $T = 5$ K. (e) Calculated STM image of *meta*-TBA molecule in the cis form on Au(111). (f) Adsorption structure corresponding to the calculated STM image in part e in a front view (left) and in a side view (right).

involve the tunneling of electrons. Further analysis of the switching process for small tip−surface distances (<10 Å) was carried out, and the changing slope in the obtained tip height versus applied voltage curves points to electronic effects. After positioning the STM tip about 6 Å above a cis isomer in a molecular island, subsequent voltage pulses for 20 s were applied. The voltage was increased by 0.1 V between subsequent pulses until the molecule under the tip had been switched. This experiment was repeated with different molecules (see Figure.4a), allowing us to extract the threshold voltage of 1.6 V at which the molecules were switched successfully. Then, pulses of this fixed voltage value ($V_m = 1.6$ V) were applied to many different cis molecules for different tip heights (4 to 6.5 Å) and times (0.1 to 20 s). During each pulse, the tunneling current was measured as a function of time (see Figure 4b). The time at

which the cis → trans isomerization occurs is detected as an abrupt change in the tunneling current (see Figure 4b). By considering the distribution of the switching times, that is, the time duration of the "high current state" for a given current, the characteristic time constant was determined using an exponential decay fit. The characteristic switching rate of the process is the inverse of the obtained switching time. By repeating this type of analysis for different currents, the dependence of the switching rate on the tunneling current was extracted. The results are shown in Figure 4c. A power dependence of the switching rate on the tunneling current was found for the current range between 0.1 and 10 nA. Such dependence is consistent with an electronically induced process for the cis → trans isomerization at small tip heights,[27] but is not expected in the case of an electric-field-induced process.

Figure 5. (a) Isolated *trans-meta*-TBA molecule on Cu(111). Image dimensions (30 × 30 Å²). (b) Overview STM image (450 × 450 Å²) of molecular adsorption on Cu(111). STM parameters are $U = 1$ V, $I = 0.2$ nA, and $T = 7$ K for part a and $U = 0.5$ V, $I = 0.1$ nA, and $T = 7$ K for part b.
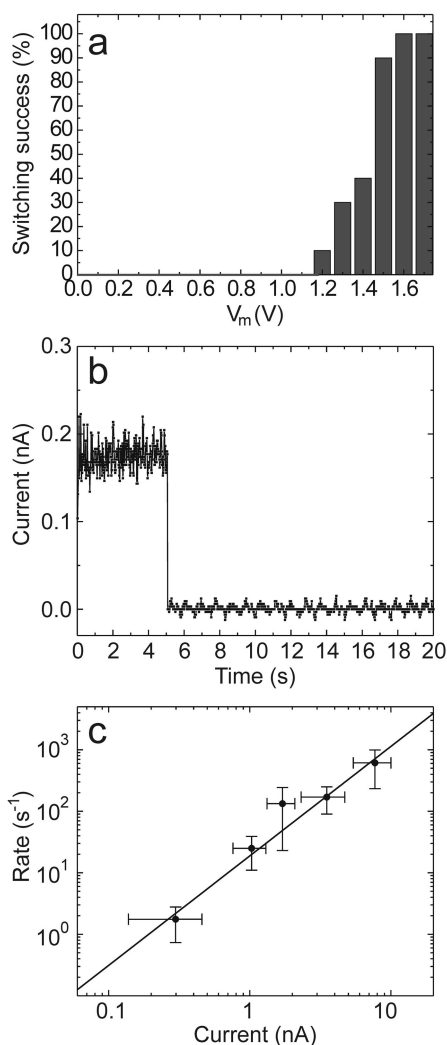
Figure 4. (a) Percentage of cis → trans switching events as a function of applied voltage. During the experiments, the tip was about 6 Å above the cis isomer and the voltage was applied for $t = 20$ s. (b) Manipulation signal versus time recorded during the application of a voltage pulse with $V_m = 1.6$ V. The sharp drop in current at 5 s corresponds to the switching of the molecule from the cis to the trans state. Note that the determination of this tunneling current drop requires an isomerization event underneath the tip. (c) Current dependence of the switching rate (extracted from the exponential decay of the event distribution with the time). The solid line is the fit of the data and corresponds to a power law: the switching rate is proportional to I^N (with $N = 1.78 \pm 0.41$). Note that the exponent N gives the number of electrons that induce the process. Taking the experimental error into account, data analysis of our results indicates either a one-electron process (e.g., excitation by a single electron or direct tunneling into an unoccupied molecular orbital) or a two-electron process (e.g., vibrational heating, if two phonons need to be excited by the electrons). The bars on the current values (i.e., along the x axis) indicate the range in which the corresponding data points are obtained.

Another indication of such an electronic effect is given by the finding that the energy position of the lowest unoccupied molecular orbital (LUMO) of *cis-meta*-TBA on Au(111), as extracted by means of scanning tunneling spectroscopy measurements,[20] matches the lowest energy one has to apply to switch the molecule from the cis to the trans state. This points to isomerization by resonant electron tunneling into the LUMO state of the molecule, if electrons are injected at suitable energies. Note that switching is also observed for the reversed bias polarity, pointing toward electron transfer from the substrate
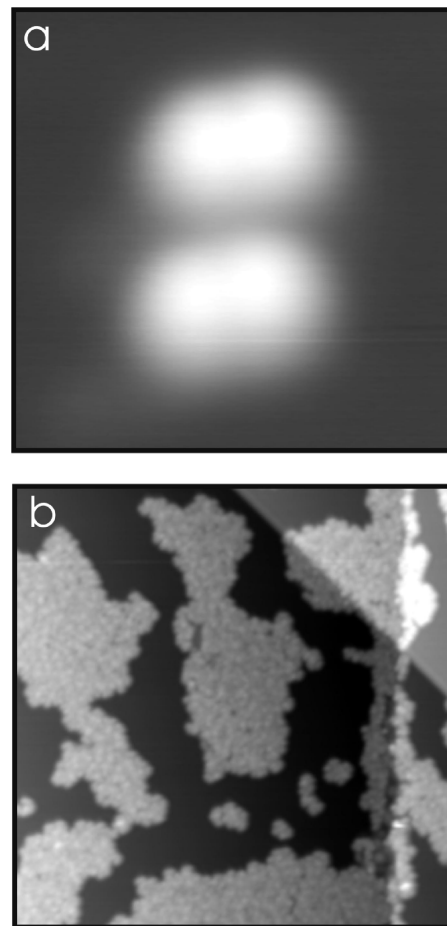
to the molecule (e.g., by hot electrons). In the present analysis, a total of 251 molecules have been switched from cis to trans; however, the trans → cis process could not be analyzed in such manner because it was found that, surprisingly, a trans isomer directly underneath the tip switches extremely rarely.

Cu(111). The important influence of the molecule−surface interaction on the isomerization process becomes apparent when comparing the above results with the behavior on Cu(111).

As on Au(111), only the trans isomer is present on this substrate after depositing *meta*-TBA molecules on Cu(111). In Figure 5a, an isolated TBA molecule on Cu(111) is shown. Its appearance resembles the one on Au(111). The four lobes correspond to the symmetrically placed *tert*-butyl groups, and the central part of the molecule is not visible. However, a different self-assembly behavior is found as a result of the modified molecule−substrate interactions. In Figure 5b, an overview STM image of molecular islands of *meta*-TBA molecules on Cu(111) is shown. It can be seen that the molecules form disordered islands on Cu(111). Molecular self-assembly at surfaces is controlled by the balance of three main factors: (i) the interplay between intermolecular forces and molecule−substrate interactions, (ii) the molecular mobility, and related to both (iii) the magnitude of the thermal energy.[28] The observation of islands of *meta*-TBA molecules on Cu(111) is therefore an indication of molecular mobility at room temperature and of an attractive van der Waals intermolecular interaction (no molecule−molecule repulsion is observed). The
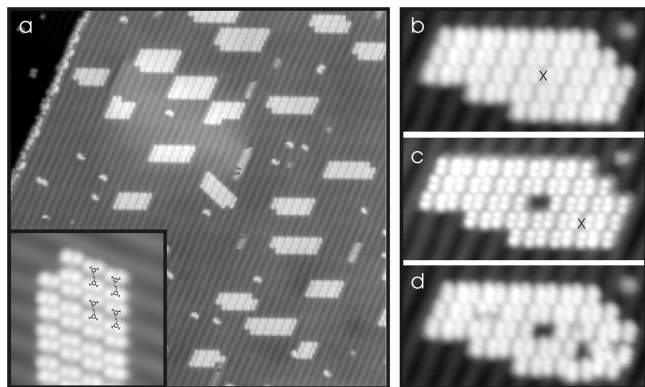
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Figure 6. (a) STM image (780 × 780 Å²) of islands of *trans-meta-*TBA molecules on Au(100). In the inset (80 × 80 Å²), a zoom out of a molecular island is shown. A model for the molecular adsorption geometry is superimposed on the STM image. (b−d) Manipulation experiment. (b) STM image before a voltage pulse is applied at the position indicated by the cross. (c) Image after the application of a voltage pulse (V_m= 2.7 V) for 20 s. A molecule has jumped onto the tip, leaving a hole in the island. At the position of the cross, another voltage pulse is applied (V_m= 3.1 V) for 20 s. (d) Image taken after the second pulse. Some molecules of the molecular island have been damaged. The isomerization did not take place. The dimensions of all three STM images of the manipulation sequence are (160 × 80 Å²). In all images, the STM parameters are $U = 1$ V, $I = 0.1$ nA, and $T = 5$ K.

lack of ordering in the islands is not related to a difference in thermal energy because the temperature of the Au and Cu substrates during depositions have been the same, but can be explained taking into account a stronger molecule−substrate interaction with respect to the Au(111) case. An ordered structure is also not obtained after annealing the sample up to 400 K. The stronger bonding to the substrate was probed by STM-induced manipulation. By applying voltage pulses to single *meta*-TBA molecules, no lateral motion or rotation of the molecules could be induced, in contrast to the *meta*-TBA behavior on Au(111) where isolated molecules always rotate or move under the influence of a voltage pulse.

Utilizing the same procedure described above for Au(111), voltage pulses were applied to *meta*-TBA molecules on Cu(111). However, in this case it was not possible to switch the molecules even by applying large voltage values (up to ±3 V). When the voltage exceeded 2.5 V, the molecules were irreversibly damaged.

Au(100). Because the molecular switching is suppressed on Cu(111), but works efficiently on Au(111), we decided to maintain gold as the substrate material but to study a different surface orientation, that is, Au(100), and its influence on *meta*-TBA adsorption and switching behavior.

An overview STM image of *meta*-TBA molecules adsorbed on Au(100) is shown in Figure 6a. The (100) surface of a gold crystal exhibits a surface reconstruction in which the topmost Au layer has switched from a quadratic arrangement to a uniformly contracted and slightly rotated hexagonal packing.[29] This reconstruction is visible in the STM images as parallel rows running along the [011] or in the perpendicular direction (there are two domains of the reconstruction).

meta-TBA molecules on Au(100) form highly ordered yet rather small islands. In each island, the same type of rows as observed in the case of Au(111) are formed, following the direction of the rows of the surface reconstruction. The central azobenzene parts of the molecules are located on the higher atomic rows of the reconstruction. The molecules are aligned

along their long axis and oriented at ±(68 ± 3)° with respect to the direction of the rows of the surface reconstruction. At the same molecular coverage and surface temperature during deposition, the dimensions of the islands on Au(100) are smaller than those in the case of Au(111). On Au(100), islands have a typical size of 10 to 40 molecules, whereas on Au(111) islands are composed of up to 10^2 to 10^3 molecules. This is an indication of a lower surface mobility presumably because of the larger substrate corrugation.

As in the case of Au(111) and Cu(111), the switching properties of *meta*-TBA molecules on Au(100) were studied by applying voltage pulses. Similarly to Cu(111), but in strong contrast to Au(111), the isomerization of *meta*-TBA molecules on Au(100) could not be induced. An example of such a switching experiment on Au(100) is shown in Figure 6b−d. Voltage pulses ranging the voltage from 1 to 2.6 V were applied to the molecular island, depicted in Figure 6b, without observing any modification of the molecular island. Voltage pulses at 2.7 V and above start to irreversibly damage the islands, and no isomerization was observed (Figure 6c and d).

The study of the tip-induced isomerization of *meta*-TBA molecules shows that the switching effect, which was observed recently on Au(111),[20] is suppressed on Cu(111) as well as Au(100). The change in the molecule−substrate interaction alters molecular self-assembly and dramatically modifies switching behavior. The dependence of the switching effect on the substrate could depend on several factors. A stronger molecule−substrate interaction caused by the Cu(111) substrate could potentially hinder the isomerization process by introducing both a larger barrier for lifting up part of the molecule and an increased steric hindrance to the necessary molecular motion imposed by the neighboring molecules. Alternatively, changes in the electronic interaction between molecules and substrate could affect the isomerization mechanism by modifying the electronic states of the trans (and cis) isomer(s) as well as the connecting transition structure(s) and therefore alter the resulting potential energy surface. Moreover, the surface corrugation might play an important role, for example, on Au(100) possessing a more corrugated surface the three-dimensional cis isomer could selectively be destabilized and therefore become inaccessible.

Conclusions

The adsorption of *meta*-TBA molecules on the Au(111), Cu(111), and Au(100) surfaces has been characterized. The appearance of the *meta*-TBA molecules in the trans and cis state in STM images is in very good agreement with calculations. After preparation, *meta*-TBA molecules are found in the trans configuration on the surface, which is the more stable configuration on the surface, independent of the chemical and geometrical nature of the surface substrate. The study of the tip-induced isomerization of *meta*-TBA molecules shows that the choice of the substrate is crucial for the ability of azobenzene derivatives to isomerize on metal surfaces. In particular, it is noteworthy that in addition to the surface's chemical composition the relative orientation of the surface atoms, that is, surface corrugation, also plays an essential role in the switching process. In the case of Au(111), where the switching is successful, the dependence of the switching rate on the tunneling current for the cis → trans isomerization at small tip heights is consistent with an electronically induced process. The detailed understanding of the interplay between molecules and substrate and its effect on switching behavior is key to the realization of molecular-based switching devices.

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