Switching of an Azobenzene-Tripod Molecule on Ag(111)

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S *Supporting Information*

ABSTRACT: The trans−cis isomerization makes azobenzene (AB) a robust molecular switch. Once adsorbed to a metal, however, the switching is inefficient or absent due to rapid excited-state quenching or loss of the trans−cis bistability. We find that tris-[4-(phenylazo)-phenyl]-amine is a rather efficient switch on Ag(111). Using scanning tunneling and atomic force microscopy at submolecular resolution along with density functional theory calculations, we show that the switching process is no trans−cis isomerization but rather a reorientation of the N−N bond of an AB unit. It proceeds through a twisting motion of the azo-bridge that leads to a lateral shift of a phenyl ring. Thus, the role of the Ag substrate is ambivalent. While it suppresses the original bistability of the azobenzene units, it creates a new one by inducing a barrier for the rotation of the N−N bond.
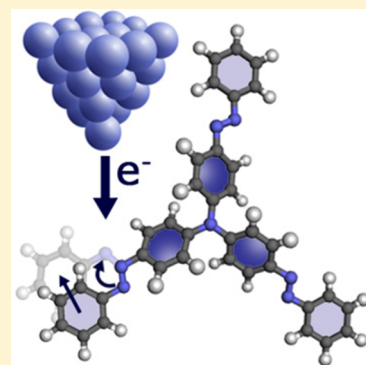
The trans−cis isomerization of azobenzene (AB) and its derivatives has been investigated in detail, partially because AB may be modified with various substituents and still exhibits robust light-driven switching.[1,2] Unfortunately, this robustness does not extend to the adsorption on metal substrates. Drastically reduced efficiencies of light-induced switching of AB when adsorbed to Au have been reported and attributed to rapid excited-state quenching.[3−8] Dispersion-corrected density functional theory (DFT) calculations have recently identified an additional factor that may be involved in reducing efficiency.[9] Once adsorbed on Au(111) or Ag(111), the barrier that prevents the cis isomer to return to the trans ground state via a rotation is drastically reduced. This effect, which may effectively eliminate trans−cis bistability, was predicted to be particularly significant on Ag(111) and more reactive substrates. An increase in the rate of thermal cis−trans isomerization of azobenzene-containing molecules has been reported from gold nanoparticles.[10,11]

Using a scanning tunneling microscope (STM), extreme current densities may be achieved through a single molecule.[12−15] Using this approach, electron-induced switching of AB derivatives on Au remains possible, although efficiencies scatter widely.[8,16−20] Despite expectations for azobenzene (AB)-containing molecules on Ag(111),[9] we find that switching of tris-[4-(phenylazo)-phenyl]-amine (TPAPA) on Ag(111) is feasible.

TPAPA comprises three AB units connected via an amino linker in a 3-fold symmetric fashion.[21−23] We demonstrate that each of the AB subunits may be reversibly and selectively switched between two states by injecting electrons. Switching may also be triggered by passing current through the central amino nitrogen atom. From scanning tunneling spectroscopy and atomic force microscopy (AFM) along with extensive density functional theory (DFT) calculations, we find that the switching is not due to a trans−cis isomerization. Rather, it involves a reorientation of the N−N bond of AB, which we suggest to proceed through a twisting motion of the azo-bridge that leads to a shift of a phenyl ring. The AB subunit is transformed between two chiral configurations that are distinct and metastable on the Ag(111) surface.

Beyond double-bond isomerization a variety of electron-induced reactions have been observed from adsorbed molecules, which encompass ring closing/opening,[24] charge transfer,[25,26] conformational isomerization,[27−30] changes of spin-state,[31,32] and ligand transfer.[33] Recent reviews may be found in refs 34−36.

The Ag(111) substrate and etched W tips were cleaned by Ar+ sputtering and annealing. The tips were further coated with silver by indenting them into the substrate. TPAPA molecules in a Ta crucible were repeatedly degassed before sublimating them at ∼150 °C onto clean Ag(111) surfaces kept at ambient temperature in ultra high vacuum (UHV). The experiments were then performed with a STM and an AFM/STM operated in UHV at ∼5 K. Differential conductance (dI/dV) spectra

were measured with a lock-in amplifier by superimposing a modulation (5−10 mV$_{rms}$, 7 kHz) onto the sample voltage V.

Figure 1a shows the structure of TPAPA on Ag(111), as predicted using dispersion-corrected DFT calculations (PBE
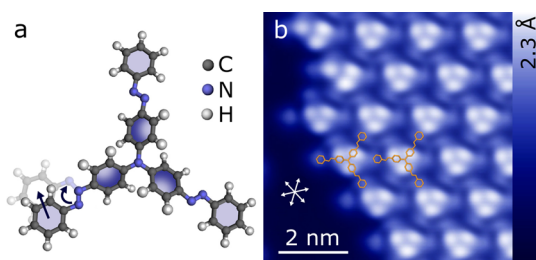

Figure 1. (a) Top view of the minimum energy structure of TPAPA on Ag(111) from DFT calculations (substrate not shown, extended models displayed in the Supporting Information). Light and dark blue indicate the outer and inner phenyl rings, respectively. The shading of the inner rings shows their ∼30° anticlockwise out-of-plane twist. The outer phenyl groups are located on the left-hand side of the plane defined by the azobenzene (AB) molecular axis and the surface normal. This handedness of the adsorbed AB subunits is denoted S. Switching of an AB subunit leads to modified structure (gray). It involves a lateral shift (arrow) of the outer phenyl ring and a twirling motion of the N−N bond (curved arrow). (b) STM topograph (1.0 V, 100 pA) of an island of TPAPA molecules on Ag(111). Scaled models are overlaid. Double-headed arrows indicate the compact directions of the Ag(111) surface.

+vdW^{surf}[37,38] using the CASTEP[39] package). We denote the phenyl groups connected via the amino nitrogen as inner (dark blue in Figure 1a) and the other ones as outer groups (light blue). Steric repulsion between the hydrogen atoms of the inner phenyls induces a propeller-like twist of the AB ligands from the molecular plane of ∼40° in gas phase and ∼30° on Ag(111).[22,23] Viewed from the center of an adsorbed molecule, the twist may be clockwise or anticlockwise, leading to a chirality of the molecule. The energetically most favorable

configuration is thereby an all-trans form, with the outer phenyl rings lying flat on the surface to maximize dispersion interaction (for more details, see the Supporting Information).

An STM topograph of a part of a TPAPA island on Ag(111) is shown in Figure 1b. Each molecule exhibits three main protrusions (∼220 pm apparent height with respect to the Ag substrate) near its center, which we attribute to the inner phenyl rings. Models are overlaid over some molecules to show their orientations, which are similar to TPAPA on Au(111).[23] In the interior of the island it is a priori not clear which set of protrusions belongs to a given molecule. The molecules at island edges, however, provide a clear indication of the position of the outer phenyl rings. The outer phenyls lead to three lower protrusions of ∼170 pm apparent height. The height at the approximate positions of the azo groups between the phenyl rings is lower by ∼20 pm. This distinct depression at the position of the N−N azo-bridge is in qualitative agreement with previous STM data from AB on metal substrates.[3,8,17,23,27,40] The average intermolecular distance extracted from STM images is (1.7 ± 0.2) nm, and the molecular lattice is rotated by (8 ± 2)° with respect to the compact directions of Ag(111). We note in passing that most islands observed were almost enantiopure.

Next, switching of TPAPA in islands was investigated. Placing the tip over an azo bridge (dot in Figure 2a) and increasing the sample voltage beyond ∼1.1 V leads to a clear change of the addressed AB subunit, as shown in Figure 2b. Currents of ∼1.1 nA were used to obtain a convenient rate of switching events. By successively repeating this procedure all three AB units were switched (Figure 2c,d). To highlight the changes in the topographs, Figure 2e−g displays difference images. They reveal little change at the molecular center and the inner phenyl rings but a drastic modification of the area of the azo bridges. Subsequently, the changes were reversed (Figure 2h−m).

Topographic changes of the outer phenyl rings are most obvious at island edges. Figure 3 shows (a,b) models of molecules at an island edge (c,d) before and (e,f) after
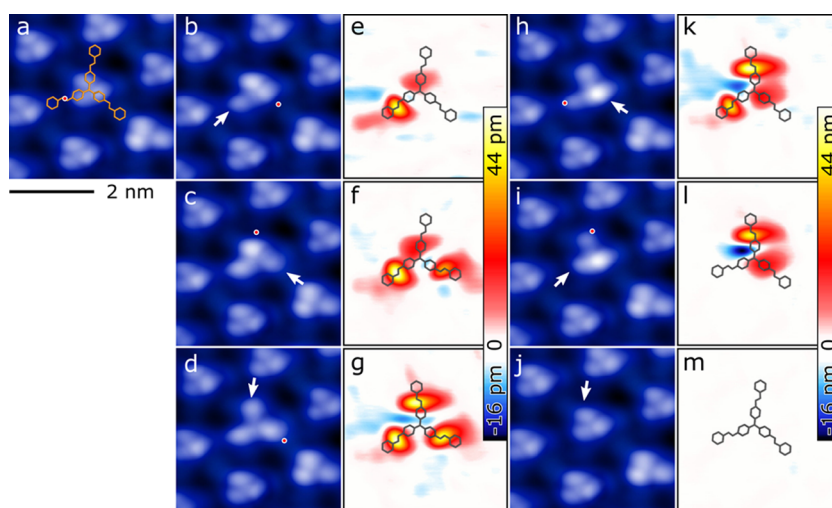

Figure 2. (a−d,h−j) Constant current topographs (1.0 V, 100 pA) from a TPAPA island. Dots indicates points of current injection for switching (V = 1.3 V, I = 1.1 nA). Arrows indicate switched AB subunits. (a) Initially the molecule at the center is in an all-trans state. (b) New state induced by passing current through the azo bridge of the AB subunit on the lower left. (c, d) New states obtained through current-induced of the remaining AB subunits. (h−j) Stepwise reversal of the switching until the original state is reached. (e−g, k−m) Difference images obtained by subtracting image (a) from (b−d) and (h−j). Scaled models of the molecule in panel a are overlaid. The largest changes in the images are localized to the positions of the azo bridges.
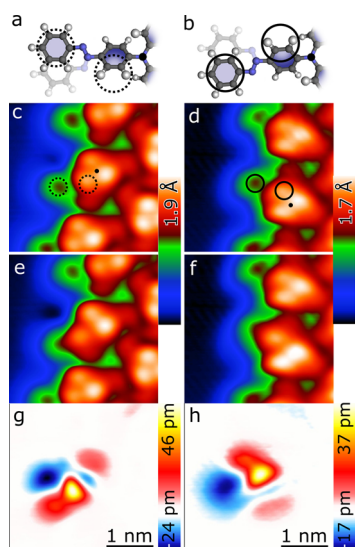
Figure 3. Switching of molecules at the edges of two islands with different molecular chiralities. Viewed from the center of a molecule, the inner phenyl rings are twisted by ~30° (a) clockwise and (b) anticlockwise. (a,b) Models show trans-configurations of one AB unit. Circles indicate the positions of protrusions observed in constant current topographs. Dots mark the N center of molecules. (c,d) Topographs (V = 1.0 V, I = 100 pA) of TPAPA at island edges corresponding to the models in panels a and b. (e, f) Topographs obtained after switching of the AB units at the island rim. (g,h) Difference images e−c and f−d.

switching. The corresponding changes are displayed in Figures 3g,h. The data confirm the apparent height change at the azo bridge and also reveal a lateral motion of the maximum due to the outer phenyl ring by ~1.5 Å. Within islands, the phenyl rings are surrounded by the tallest features of neighboring molecules. This renders a quantitative determination of the lateral shift from constant-current images more difficult. At first glance, the shift actually appears to be smaller; however, when the superposition of the currents to the relevant phenyl ring and the neighbor is taken into account, a consistent shift is found (see the Supporting Information).

Switching may also be induced by passing current through the center of a TPAPA molecule. Time series of the current (Figure 4) reveal abrupt current fluctuations between four levels, which (in a sequence of increasing currents) correspond
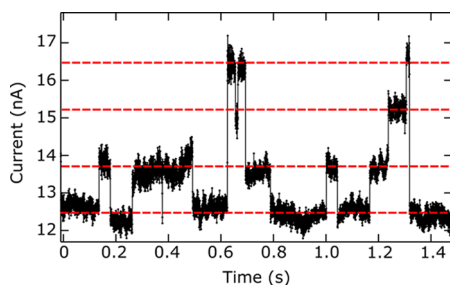

Figure 4. After placing the tip over the center of a TPAPA molecule, the current feedback was disabled and time series of the current were measured at selected sample voltages. Abrupt current fluctuations occurred. The example shown was recorded at V = 1.5 V and reveals four distinct current levels indicated by dashed lines. The lowest level is observed on all-trans TPAPA. Increasing levels reflect 1, 2, and 3 switched azobenzene subunits.

to the pristine molecule and the states with 1, 2, or 3 switched AB units. The data demonstrate that the switching is reversible; however, because current is injected at the center of the TPAPA molecule, there is no preference for a specific AB subunit. Selectivity for a specific AB subunit is achieved by injection into a N−N bond, as demonstrated in Figure 2.

Switching occurs at both bias polarities with yields varying from $Y \approx 10^{-13}$ (at V = 0.8 and −1.8 V) to $Y \approx 10^{-11}$ at elevated currents and voltages (see SI for details). At positive sample voltage, the switching rate approximately follows a power law $\approx I^2$, which may indicate a two-electron process.

The most obvious switching process to consider for AB and its derivatives is trans−cis isomerization; however, we exclude this possibility in the present case for two reasons. First, trans−cis isomerization significantly modifies the electronic states of AB in the gas phase and also on surfaces.[3,8,27,40,41] dI/dV spectra of pristine and switched TPAPA measured at characteristic positions (Figure 5), however, reveal merely
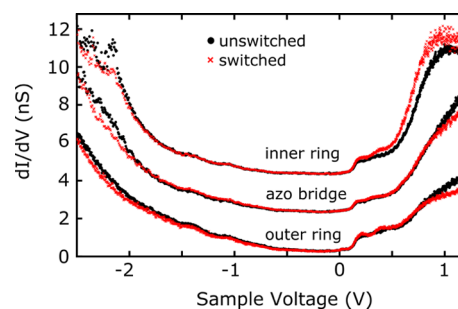

Figure 5. Differential conductance (dI/dV) spectra acquired above the inner and outer phenyl rings and the azo bridge of an AB subunit of TPAPA. Data were recorded from a pristine all-trans molecules and a switched isomer. Current feedback was opened at V = −0.1 V and I = 500 pA. The spectra are vertically offset by 0, 2, and 4 nS for clarity. The data indicate positive and negative ion resonances that vary little between the isomers.

minor differences between the switched and pristine states. Second, our DFT calculations revealed a number of stable cis states (three shown in the SI, Figure S6), all of which involve significant geometrical and electronic changes compared with the trans state. As detailed later, none of these changes are consistent with our experimental data, which suggests a much more subtle structural and electronic change upon switching.

Figure 6a shows a constant-current STM image of molecules with varying numbers of switched AB subunits. Because constant-current STM images may be affected by electronic effects, we performed additional measurements combining STM and noncontact AFM at submolecular resolution. Figure 6b,c displays AFM frequency shift data and a current map measured at constant tip height above the substrate. In the stable cis conformations identified via DFT (see SI), the outer phenyl rings are either strongly laterally displaced or switched to a tilted or almost vertical arrangement on the surface. These geometries are incompatible with the low contrast of the outer phenyl rings in the AFM data of Figure 6b. Rather, these data indicate that the inner rings protrude farthest from the surface, whereas the outer ones appear to lie rather flat. On the basis of the current map of Figure 6c, where the outer rings, the inner rings, and the central amino linker form a straight line, this scenario can be excluded.
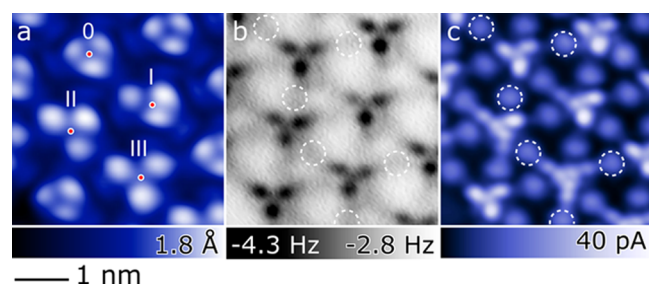
Figure 6. (a) Constant−current topograph (1 V, 100 pA). Molecules labeled **0** to **III** exhibit zero, one, two, and three switched AB subunits. (b) AFM frequency shift data from the same area measured at constant tip height. (Amplitude of cantilever oscillation 1 Å.) The positions of the outer rings are marked with dashed circles. While a significant frequency shift is found above inner phenyl rings the outer rings and the azo bridge cause hardly any contrast. (c) Current map recorded at constant tip height from the same area.

Another possible switching mechanism is a lateral shift of an outer phenyl ring. The outer phenyl rings can be situated either to the left or to the right of the plane defined by the azobenzene molecular axis and the surface normal. This reflects a handedness (denoted S and R, respectively) of the adsorbed AB subunits. DFT calculations yield metastable surface geometries for R and S conformers of an AB subunit of TPAPA. When the inner phenyl rings are twisted anticlockwise, the S configuration is minimally more stable. This higher stability is associated with a change in height of almost 0.6 Å of the N atom in the azo-bridge, which is bound to the inner phenyl ring. The corresponding isomerization reaction requires a torsional motion of the nitrogen atoms in the azo-bridge. We propose that this rearrangement involves a twisting motion of the central nitrogen atoms around each other coupled to a lateral shift of the outer phenyl ring rather than a rotation that lifts the outer phenyl ring out of the surface plane. The calculated energy barrier height for this process is 0.47 eV. This value is consistent with the experiments where significant switching rates were observed at bias voltages of 0.8 V and above.

An out-of-plane rotation of a single phenyl ring has been reported from 3,3′-dicyanobenzene (dimeta-cyanobenzene, DMC) on Au(111).[27] We do not favor this mechanism in the present case of TPAPA on Ag(111). According to our DFT +vdW^{surf} calculations it exhibits a significantly higher barrier due to the additional energy penalty of losing the dispersion interactions between phenyl ring and surface.

The localized change in apparent height and tunneling conductance as observed in the STM can therefore be understood as a conformational switching from an S to an R state and a corresponding uplifting of the central azo-bridge at almost minimal lateral displacement of the phenyl groups. Much in accordance with the measured dI/dV curves, this conformational switching occurs with minimal modification of the energetic position of the molecular orbitals with respect to the Fermi level.

In summary, the three azobenzene units of the compound TPAPA on Ag(111) may each reversibly be switched between two distinct states. Switching is triggered by passing current through the center of a molecule or, to achieve selectivity, through the azo bridges. The efficiency of the process is comparable to molecular switching of AB derivatives that were decoupled from a Au substrate by spacer groups;[3,18,40] however,

the switching does not involve the trans and cis isomers of AB that were predicted to lack of bistability on Ag(111). It rather involves a lateral motion of a phenyl ring and a twisting motion of the azo bridges. Thus, the role of the Ag substrate is ambivalent. While it suppresses the original bistability of azobenzene it creates a new switching function that is based on surface-induced chirality.

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Notes

The authors declare no competing financial interest.

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(16) A detailed comparison of data from different derivatives is difficult because varying bias voltages and currents have been used. For instance, for AB on Au(111) a switching yield per electron $Y \approx 10^{-18}$ at − 1.5 V and 0.5 nA was reported,[8] for anilino-nitro AB on Au(111) $Y \approx 10^{-9}$ at 2.5 V and 0.5 nA,[19] for 4-(4-nitrophenylazo)aniline on Au(111) $Y \approx 10^{-8}$ at 0.7 V,[17] for *trans−cis* isomerisation of dihydroxy-AB adsorbed on NaCl the yield is $Y \approx 10^{-8}$ at 0.7 V,[20] and for tetra-*tert*-butyl AB on Au(111) $Y \approx 10^{-8}$ at 1.6 V, 0.5 nA, increasing to $Y \approx 10^{-7}$ at 1.6 V, 2 nA.[18]

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