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

Katharina Scheil, Thiruvancheril G. Gopakumar, Julia Bahrenburg, Friedrich Temps, Reinhard Johann Maurer, Karsten Reuter, and Richard Berndt

1Institut für Experimentelle und Angewandte Physik, Christian-Albrechts-Universität, 24098 Kiel, Germany
2Department of Chemistry, Indian Institute of Technology Kanpur, Kanpur 208016, India
3Institut für Physikalische Chemie, Christian-Albrechts-Universität, 24098 Kiel, Germany
4Lehrstuhl für Theoretische Chemie, Technische Universität München, 85747 Garching, Germany

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. 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. Dispersion-corrected density functional theory (DFT) calculations have recently identified an additional factor that may be involved in reducing efficiency. 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. Using a scanning tunneling microscope (STM), extreme current densities may be achieved through a single molecule. Despite expectations for azobenzene (AB)-containing molecules on Ag(111), 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. 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, charge transfer, conformational isomerization, changes of spin-state, and ligand transfer. Recent reviews may be found in refs.

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

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were measured with a lock-in amplifier by superimposing a modulation (5–10 mV<sub>rms</sub>, 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 +vdW<sub>surf</sub> using the CASTEP 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 phenyl groups connected via the amino nitrogen as inner (dark blue) and the Ag(111) surface. 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 (\( \sim 220 \) 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 \( \sim 170 \) pm apparent height. The height at the approximate positions of the azo groups between the phenyl rings is lower by \( \sim 20 \) 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 (\( 1.7 \pm 0.2 \) nm, and the molecular lattice is rotated by (\( (8 \pm 2)^\circ \)) 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 \( \sim 1.1 \) V leads to a clear change of the addressed AB subunit, as shown in Figure 2b. Currents of \( \sim 1.1 \) 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...
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 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 $\approx I^3$, 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. $dV/dI$ spectra of pristine and switched TPAPA measured at characteristic positions (Figure 5), however, reveal merely minor differences between the switched and pristine states. Second, our DFT calculations revealed a number of stable cis isomers (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 4a 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.
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). We do not favor this mechanism in the present case of TPAPA on Ag(111). According to our DFT +vdW* 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; 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.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacslett.6b01011.

- SI-1: Current dependency of switching rate. SI-2: Lateral shift of phenyl within islands. SI-3: Details of dispersion-corrected density functional theory calculations. (PDF)

### AUTHOR INFORMATION

*Corresponding Author*

E-mail: berndt@physik.uni-kiel.de.

**Notes**

The authors declare no competing financial interest.

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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 ≈ 10–18 at −1.5 V and 0.5 nA was reported,8 for anilino-nitro AB on Au(111) Y ≈ 10–17 at 2.5 V and 0.5 nA,9 for 4-(4-nitrophenylazo)aniline on Au(111) Y ≈ 10–8 at 7.0 V,10 for trans-cis isomerisation of dihydroxy-AB adsorbed on NaCl the yield is Y ≈ 10–7 at 0.7 V,9 and for tetra-tert-buty1 AB on Au(111) Y ≈ 10–7 at 1.6 V, 0.5 nA, increasing to Y ≈ 10–7 at 1.6 V, 2 nA.8


