

Reversible Photo-Switching of Single Azobenzene Molecules in Controlled Nanoscale Environments

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ABSTRACT

We drive reversible photoinduced switching of single azobenzene-functionalized molecules isolated in tailored alkanethiolate monolayer matrices on Au{111}. We designed molecular tethers to suppress excited-state quenching from the metal substrate and formed rigid assemblies of single tethered azobenzene molecules in the domains of monolayer to limit steric constraints and tip-induced and stochastic switching effects. Single molecules were reversibly photoisomerized between *trans* and *cis* conformations by cycling exposure to visible and UV light. *Trans* and *cis* conformations were imaged as high (2.1 ± 0.3 Å) and low (0.7 ± 0.2 Å) protrusions in STM images and were assigned to the on and off states of the molecule, respectively.

A major challenge of molecular electronics is to design and to incorporate single molecules as transistors, diodes, or switches into circuits.^{1–5} Molecular switches are typically regulated by electric field,^{6–8} a scanning tunneling microscope (STM) tip,^{9–12} or by chemical/electrochemical reaction.¹³ These activation methods are relatively slow, may interfere with the function of nanosized circuits, and can impose limitations on device applications. However, far-field illumination or other stimuli are more feasible driving factors to power nanoscale switches^{14–16} because of the ease of addressability, picosecond response time, and compatibility with a broad range of ambient environments, such as solvents, electrolytes, or gases. Therefore, photochromic molecules that can reversibly photoswitch between two different conductance states could serve as more practical molecular switches. Azobenzenes, which can reversibly isomerize between *cis* and *trans* forms under photoillumination, have been studied to control their switching on metal electrodes.^{17–19} Other molecules that have been studied for their photochromic switching are diarylethenes^{20–23} and stilbenes.²⁴ However, evidence of photoinduced switching

of single molecules on metal electrodes is often complicated by surface quenching,^{18,23} steric hindrance, and nonphoto-induced switching.^{10–12,17–19,23,25–27} In most single-molecule switching studies, active molecules have been attached at domain boundaries and vacancy islands of host alkanethiolate matrices. Since molecules attached at domain boundaries and vacancy islands are loosely packed and less stable, they are influenced by fluctuations^{10,12,26} and therefore switch randomly because of nonphoto-induced effects.

The development of a practical molecular-scale optoelectronic device will also require control over switching in ambient conditions (atmospheric pressure and room temperature). However, such control over reversible switching has not been achieved in ambient^{17,19,23} nor under ultrahigh vacuum or cryogenic temperatures.¹⁸ Here, we report reversible photoswitching of azobenzene-functionalized single molecules (**1**) when assembled on Au{111}. Control was achieved in ambient conditions by appropriately designing the tether and tuning the rigid assembly of the molecule to limit surface quenching and nonphoto-induced switching effects.

Surface quenching is dependent upon photoinduced electron transfer from an excited state of a photochromic molecule to the gold substrate.²⁸ If electronic coupling between the molecule and the substrate is strong, the excited state is quenched, and isomerization does not occur. To overcome this problem, Comstock et al. attached *tert*-butyl

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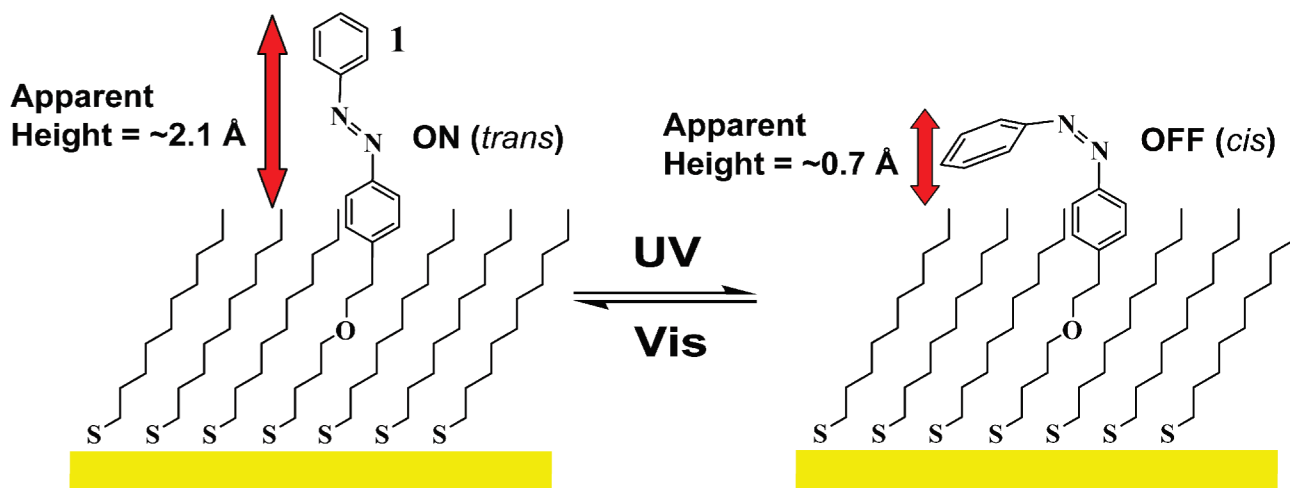
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Scheme 1. Isolated Azobenzene-Functionalized Single Molecules (**1**) Embedded in 1-Decanethiolate (**C10**) SAM Films on Au{111}^a



^a Photo-induced changes in apparent height of the azobenzene-functionalized molecules in STM images due to isomerization of the azobenzene moiety between *trans* and *cis* are defined as on (apparent height = 2.1 ± 0.3 Å) and off (apparent height = 0.7 ± 0.2 Å) states, respectively.

legs to an azobenzene moiety to reduce coupling.¹⁸ These molecules were irradiated for long periods (~3 h) under cryogenic and ultrahigh vacuum conditions and yet only partial isomerization and one reversible switching event were observed. Furthermore, the events were convoluted by stochastic or tip-induced switching.

Steric constraints of tightly packed matrixes can restrict conformational changes, thus hindering isomerization in azobenzenes. Pace et al. used a self-assembled azobenzene monolayer and irradiated the surface with UV light to observe photoisomerization.¹⁹ On the basis of the changes in contrast in the images, they concluded that there must have been photoisomerization of the monolayer. They did not observe any changes in packing density, suggesting high steric hindrance that would restrict the conformational changes expected in the molecule upon isomerization. We note that such contrast changes in STM images are also commonly produced by tip-induced effects.^{29,30}

Here, we designed an azobenzene-functionalized molecule, 4-[2-(4-phenylazo-phenyl)-ethoxy]-butane-1-thiol (**1**, shown as the thiolate), to chemisorb within domains of decanethiolate (**C10**) self-assembled monolayers (Scheme 1).³¹ Rigid assembly of **1** surrounded by **C10** molecules minimizes conformational changes at and near the gold–sulfur bond (as opposed to the case of molecules adsorbed at defects such as domain boundaries). The molecular design renders stability due to favorable intermolecular interactions with the monolayer and reduces steric constraints as well as electronic coupling between the excited-state orbitals of the molecule and the Au substrate. The molecular tethering scheme allows the azobenzene moiety to protrude from the **C10** matrix (Scheme 1), minimizing electronic coupling as well as steric hindrance. Previously, it was shown that electronic coupling can be reduced by increasing the length, replacing methylene link by an ether link,³² and reducing the π conjugation of the tether.^{33,34} Hence, by minimizing steric hindrance, surface quenching, and nonphotoinduced switching effects, isolated molecules of **1** attached to Au{111} could be controlled and reversibly switched between on and off states by irradiation

under ambient conditions (*vide infra*). We correlated these states with *trans* and *cis* isomers of the azobenzene, respectively.

Single molecules were prepared on Au{111} by including them in the domains of the **C10** monolayer through coassembly. An ethanolic mixture of **1** and **C10** were coadsorbed with a total thiol concentration of 1 mM and a molar ratio of 1:4, respectively, for 24 h under a nitrogen atmosphere. The sample was then annealed in **C10** vapor (for 2 h at 80 °C) to add matrix molecules to increase the packing and order of the matrix.³⁵ A custom-made STM operating under ambient conditions was used for imaging. The density of single molecules within the domains was consistent throughout the sample, and these were imaged as 2.1 ± 0.3 Å apparent protrusions from the **C10** matrix, defined as the on state (for tunneling conditions of 1 V sample bias and 2 pA tunneling current). When imaged continuously for an hour without illumination, no switching events were observed (Supporting Information, Figure 1). We then scanned the same sample with a range of bias polarities (1.0 to –1.0 V) (Supporting Information, Figure 2), and again, no switching events were observed. Thus, the designed tether and the new assembly limit the molecules' ability to switch stochastically or by tip-induced effects, in contrast to what we previously observed for oligo(phenylene-ethynylene) molecules when allowed conformational freedom at domain boundaries and other defects.^{10–12,25–27}

Isolated molecules within domains were exposed to ultraviolet (UV) light (~365 nm) and imaged with STM at increasing UV illumination times. Molecules switched to the off state, characterized by an apparent height reduction of ~1.4 Å (Figure 1). We observed that increasing numbers of molecules were switched with longer UV illumination times. The off state of **1** appeared to protrude 0.7 ± 0.2 Å above the **C10** matrix in STM images at these tunneling conditions (1 V sample bias, 2 pA tunneling current). Figure 1B–E shows molecules switching from the on to the off state after 10, 35, 60, and 160 min, respectively, of UV exposure. The number of molecules switched as a function of exposure time

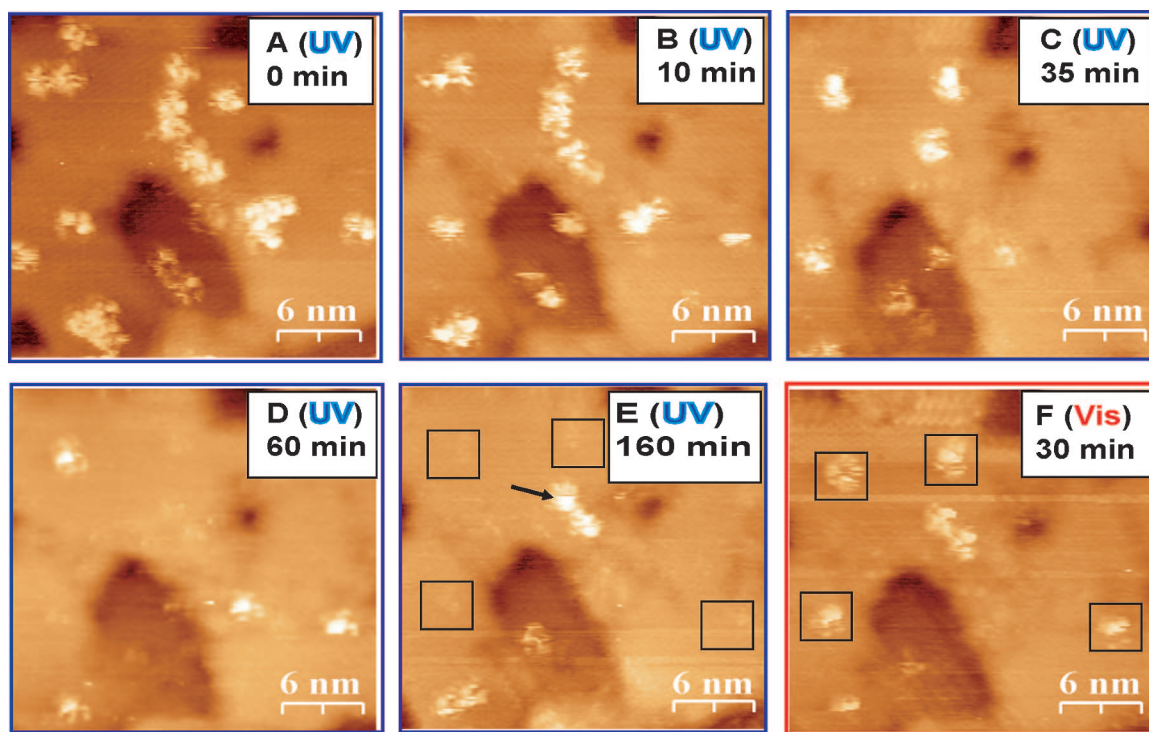


Figure 1. Azobenzene-functionalized molecules switch off and switch on upon irradiation with ultraviolet (~ 365 nm) and visible (~ 450 nm) light, respectively. Images are recorded after irradiating (A) 0 min, (B) 10 min, (C) 35 min, (D) 60 min, and (E) 160 min with ultraviolet light and visible light irradiation for (F) 30 min. A–E show switching off of single molecules with continued UV illumination. The squares in E and F show switching on of molecules with visible illumination. The arrow in E shows switching on of a molecule with UV illumination. Scanning tunneling microscope (STM) images are recorded at $V_b = 1$ V and $I_t = 2$ pA. Contrast changes in the different images are due to STM tip changes during imaging.

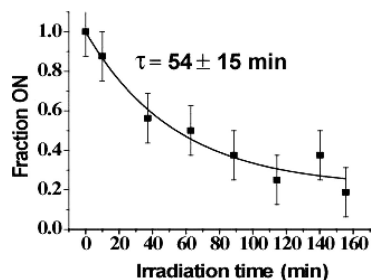


Figure 2. Fraction of azobenzene-functionalized molecules in the on state decreases as a function of time of ultraviolet irradiation (~ 12 mW/cm²). The decay constant (τ) under these conditions is 54 ± 15 min.

shows an exponential time dependence with a decay constant of 54 ± 15 min (Figure 2) under these conditions (~ 12 mW/cm²). The error bars are determined by the standard deviations of the observed numbers of molecules in three sets of observations. The slower decay constant as compared to that in solution is likely due to the electronic coupling of the azobenzene moiety with the Au substrate, which is reduced by the inclusion of the tether, but still appears to be significant in deactivating isomerization. Previously, in an ensemble measurement, Weisner et al.³⁶ also demonstrated an exponential dependence of azobenzene photoisomerization on illumination time. The exponential time dependence and elimination of other potential switching effects indicate that, here, photoexcitation causes switching and that it is based on photoisomerization. All of the protrusions in the images (Figure 1A–F) represent molecules of **1** and are found only

when **1** is coassembled with the matrix. The similarities of the shapes and sizes of the protrusions in each image suggest that each protrusion corresponds to a single molecule; the shape and size of each is a map of the STM tip and some of the contrast changes in different images are due to STM tip changes during imaging.³⁷

Theoretical calculations predict the *trans* isomer of azobenzene to be $\sim 100\times$ more conductive than the *cis* isomer.³⁸ When **1** isomerized from *trans* to *cis* on Au{111} (as shown in Scheme 1), the actual height, in contrast to apparent height, decreases by ~ 4 Å³⁹ because of the conformational changes about the N–N double bond. Hence, both conductivity and height contribute to the observed reduction in apparent height (on to off, *trans* to *cis*), since STM images are a convolution of physical height and electronic structure.

After 160 min of UV illumination, more than 90% of the azobenzene-functionalized molecules isomerized from *trans* to *cis*. Subsequent illumination with visible light (~ 450 nm, ~ 6 mW/cm²) for 30 min switched nearly 50% of **1** back to the on state (Figure 1F). The squares in Figure 1E,F highlight a few switching on events. In the gas and solution phases,^{40,41} visible light is known to photoisomerize azobenzene from *cis* to *trans*; hence, we conclude that the azobenzene-functionalized molecules have been reversibly photoswitched at the single-molecule level.

The reversibility of photoswitching was further established by comparing the apparent height profiles of molecules¹⁰ on

the sample before and after exposure with UV and visible light. Nearly ~ 150 molecules were sampled before and after UV irradiation (to switch to the off state) and after visible illumination (to switch to the on state), and the apparent heights were plotted. Drift arising from thermal fluctuations induced by light and creep in the STM piezoelectric imaging mechanism makes it difficult to observe a single feature for very long times (greater than 5 h). Several STM image frames of a scan area $800 \text{ \AA} \times 800 \text{ \AA}$ with ~ 30 – 40 azobenzene-functionalized molecules in each were used to collect apparent height changes. The apparent heights before UV, after UV, and after visible illumination are $2.1 \pm 0.3 \text{ \AA}$, $0.7 \pm 0.2 \text{ \AA}$, and $1.6 \pm 0.3 \text{ \AA}$, respectively. After visible illumination, the sample includes both on and off molecules, thus, giving a lower apparent height distribution compared with the initial on state.

Figure 1E (arrow) shows a molecule in the on state, which was off in Figure 1D even after UV illumination. The absorption band of *cis* molecules overlaps with UV light, and thus, irradiation with UV for sufficiently long times (1–2 h) occasionally triggers isomerization from *cis* to *trans*.⁴⁰ Figure 1F (squares) shows reversibly switching on $\sim 50\%$ of the total off molecules after visible illumination for 30 min. Thermal *cis*–*trans* isomerization of azobenzene has been reported to take place on timescales of 10–30 h,⁴² but we observed some switching in 30 min (Figure 1E,F). The visible light, with an intensity ($\sim 6 \text{ mW/cm}^2$) lower than that of typical ambient light, is too weak to induce significant heating that could thermally isomerize the azobenzene moiety. Thus, on the basis of our observations of fast response of switching compared with thermal isomerization and kinetic studies by Liu et al.,⁴² isomerization of *cis* to *trans* here is photoinduced rather than due to thermal relaxation.

In conclusion, we showed that the molecular tether and assembly isolated the azobenzene moiety from the metal substrate and rigid assembly of **1** within the domains of the host matrix rendered stability, due to which control over reversible photoswitching was achieved. Such rigid assembly can potentially be utilized in stabilizing single molecules for other switching studies in which the matrix plays a key or interfering role. With stability in ambient and improved understanding of photoswitches, assembly of practical molecular devices may become possible. In order to test these ideas, we are now studying assemblies of these photo-switches.

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Supporting Information Available: Supplementary Figure 1: With time (1 h), but no illumination, no change in apparent height was observed in scanning tunneling microscope images while recording under similar conditions ($I_t = 2 \text{ pA}$; $V_s = 1.0 \text{ V}$) to those used to record Figure 1.

Supplementary Figure 2: With sample bias polarity (V_s) change (but still no illumination), (a) 1.0 V to (b) -1.0 V , no significant change in apparent height was observed ($I_t = 2 \text{ pA}$) in scanning tunneling microscope images. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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