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Light-Powered Electrical Switch Based on Cargo-Lifting Azobenzene Monolayers**

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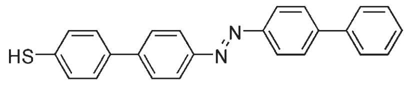
Inspired by the complex molecular machines found in nature, chemists have developed much simpler molecular motors.[1–3] Among them, several systems incorporating azobenzene have been proposed, which exploit the reversible *trans–cis* isomerization triggered by light[4] or an electric field[5] for applications such as optical data-storage devices,[6] switchable supramolecular cavities, and sensors.[7] Recently, it has been demonstrated that the photoisomerization process of individual polymer chains incorporating azobenzenes can express mechanical work.[8] In light of these findings, one can foresee self-assembled monolayers (SAMs)[9,10] of aromatic azobenzenes as molecular systems able to express forces of unprecedented magnitude by exploiting a collective subnanometer structural change.

We recently designed a rigid and fully conjugated azobenzene exposing a thiol anchoring group,[11] which was able to form a tightly packed SAM on Au(111) (SAM_{AZO}). Scanning tunneling microscopy (STM) studies revealed that upon light irradiation of the chemisorbed SAMs, a collective isomerization of entire molecular-crystalline domains occurred with an outstandingly high directionality.[11] Based on these results, a cooperative nature of the isomerization of adjacent AZO molecules has been proposed. Furthermore, the joint action of the molecules in the SAM provides an ideal system as a potential "cargo" lifter.



AZO

Herein, we show that, upon irradiation, azobenzene SAMs incorporated in a junction between an Au(111) surface and a mercury drop are able to 1) lift the "heavy" Hg drop, and 2) reversibly photoswitch the current flowing through the junction (Figure 1).

Current–voltage (*I–V*) characteristics averaged over more than 30 junctions incorporating AZO SAMs in the *trans* and the *cis* conformations are shown in Figure 2a. The SAM_{AZO} in the *cis* conformation was obtained with extremely high yield (98%) upon irradiation by UV light of the SAM_{AZO} initially formed by the *trans* conformer.[11] The difference in the measured currents, which amounts to about 1.4 orders of magnitude, is in agreement with a through-bond tunneling mechanism described by Equation (1).[13]

$$I = I_0\, e^{-\beta\Delta d} \tag{1}$$

Accordingly, the observed current values fit well assuming a decay factor ($\beta = 0.5 \pm 0.1$ Å^{-1}) comparable to that for polyphenyl chains[12] and a difference in thickness between SAMs containing the *trans* and *cis* forms of about $\Delta d = d_{trans} - d_{cis} \approx 7$ Å.

The most significant results were obtained on the SAM_{AZO}-based junctions, upon alternating the wavelength of in situ irradiation of the SAM_{AZO} through the transparent Au surface. As displayed in the *I–V* curves in Figure 2b, starting from the SAM_{AZO} junction in its *trans* conformation, the current density increases and decreases reversibly over one order of magnitude upon alternating irradiation at λ = 370 and 450 nm, respectively. The reversible character of the photoinduced current variation provides unambiguous evidence for the stability of the Au(111)-SAM_{AZO}//SAM_{C12}-Hg junction. In particular, the reversibility of the values rules out an interdigitation of the C_{12} SAMs exposed on the Hg drop with the SAM_{AZO} chemisorbed on the Au(111) surface.

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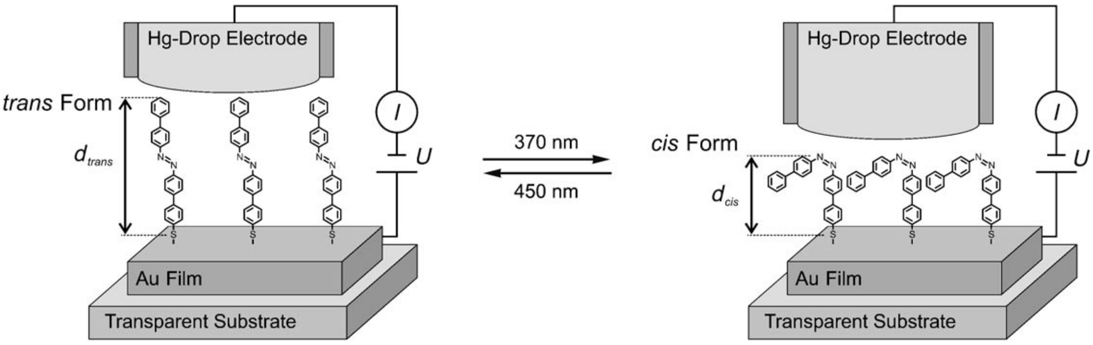

Figure 1. The SAM_{AZO} immobilized between a transparent Au surface and a Hg drop electrode. As a result of the light-triggered isomerization between the rodlike *trans* isomer (left) and the more compact *cis* isomer (right), the distance between both electrodes varies, thus providing both an optoelectronic switch and an optomechanical cargo lifter. To demonstrate and exploit this collective effect, a metal–molecule–metal junction was used (see the Supporting Information), based on a Hg top electrode. Hg was chosen because it is a metal featuring a compliant liquid surface.[12] The junction incorporates the SAM_{AZO} chemisorbed on a 25-nm-thick semitransparent Au(111) electrode on a quartz support and a Hg drop coated with a SAM of dodecanethiol as the top electrode.

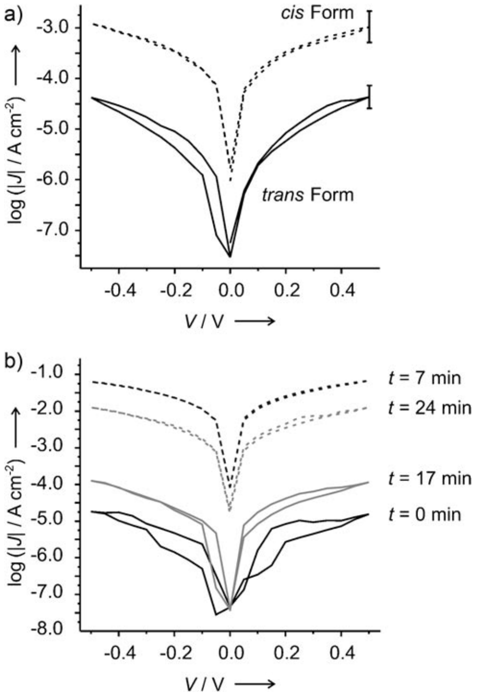

Figure 2. Light-induced switching of the electrical properties of the SAM_{AZO}. a) *I–V* curves measured in Au-SAM_{AZO}//SAM_{C12}-Hg junctions formed ex situ. Results for the SAM_{AZO} in the *trans* and *cis* forms are shown as blue and red lines, respectively. b) *I–V* curves recorded in situ on an Au-SAM_{AZO}//SAM_{C12}-Hg junction incorporating the *trans* isomer and subsequently irradiated with alternating wavelengths at $\lambda = 370$ and 450 nm, as indicated.

Importantly, similar differences in current were obtained upon in situ (Figure 2b) and ex situ (Figure 2a) irradiation. The data of Figure 2 indicate that the reversible *cis–trans* photoconversion exhibits the same high yield in both in situ and ex situ experiments. The results therefore demonstrate that the SAM_{AZO} is able to keep the electrical contact with the upper C_{12}-SAM-stabilized Hg electrode upon repeated cycles, as a loss of electrical contact would have resulted in a lower current for the *cis* isomer with respect to the *trans* isomer.

The switching behavior can be explained in terms of the SAM_{AZO} reversibly lifting and lowering the Hg drop on top of the monolayer. Taking into account the radius of the spherical drop (ca. 1.5 mm) and the density of Hg (13546 kg m^{-3}), switching the SAM_{AZO} from the *cis* to the *trans* isomer must lift a mass of 1.9×10^{-4} kg a distance of Δd. The total force per unit area exerted by the Hg on the SAM_{AZO} is 1.0×10^{5} N m^{-2}; this value is calculated based on a simple force balance that accounts for gravitational effects, atmospheric pressure, and surface tension (see the Supporting Information for details). Assuming that the surface packing density of the SAM_{AZO} is 4.0×10^{18} molecules m^{-2} (as obtained from the size of the unit cell of the SAM_{AZO} detected by STM[11]), the average force exerted by the Hg on an individual AZO molecule in the SAM amounts to $F_M = 2.6\times10^{-14}$ N. The joint forces per unit area generated by the molecules in the SAM_{AZO} sum up to at least 1.0×10^{5} N m^{-2}, which is large enough to lift or displace the Hg drop. Comparison of this force with that determined by Gaub for each molecule,[8] which amounts to 10^{-12} N, indicates that the system is still far from exploiting its full potential.

Our results demonstrate a proof of principle: by harnessing the collective nature[11] of the isomerization in adjacent highly rigid AZO molecules, it is possible to photoswitch the current through a molecular junction and to develop a prototypical molecular machine that acts as a cargo lifter. Therefore, our system holds potential as a photoswitchable monolayer for nanoelectronics, for example, for diodes and transistors.[14–17] Furthermore, these findings pave the way towards the fabrication of a new class of devices based on the force expressed by molecules organized in films, and towards optically switchable nanoelectronic circuitry.

Experimental Section

Transparent gold surfaces: Au(111) substrates were prepared by evaporating 25 nm of gold onto quartz slides (or freshly cleaved mica) after preheating the quartz at 400 °C for 3 h. Thermal deposition was performed at a rate of 0.01 nm s^{-1} and a pressure of 8–9×10^{-7} Torr.

Monolayer preparation: The SAMs were formed by immersion of freshly prepared substrates of Au into a solution (0.1 mM) of AZO in degassed chloroform at room temperature for 24–48 h. After immersion, the samples were carefully rinsed with pure chloroform and blown dry with argon. No evidence of impurities or oxidative degradation products was found.

Electrical measurements: Current–voltage measurements were performed on the junction (depicted in the Supporting Information), which was assembled as follows. A Hg drop was extruded from a syringe and placed in a solution (1 mM) of dodecanethiol in ethanol to form a SAM (SAM_{C12}-Hg). By making use of a micromanipulator, the SAM_{C12}-Hg electrode was brought into contact with the Au surface that exposed the SAM_{AZO}, while immersed in hexadecane. For each electrical measurement, the contact area of the junction was evaluated to calculate the current density. The contact area was determined to be 2×10^{-7} mm^2 from an image of the Hg drop collected by a camera with 40× magnification.

Photoirradiation experiments: The photoisomerization of AZO SAMs was studied by irradiating the SAM under investigation through the transparent gold surface. To obtain the same intensity of light reaching the AZO SAMs in the ex situ (irradiation of the SAMs without assembling the junction) and in situ (irradiation of the SAMs in the assembled junction) experiments, the gold surfaces carrying the SAMs had the same thickness. For details, see the Supporting Information and reference [11].

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