

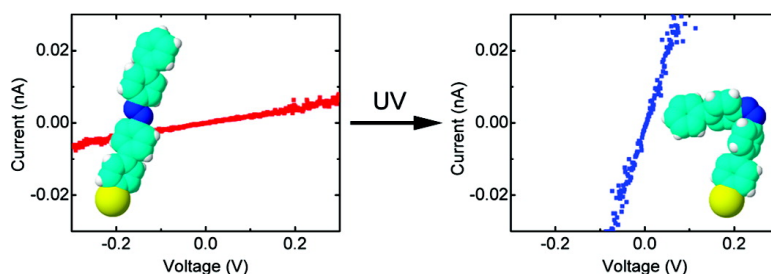
Communication

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Azobenzenes as Light-Controlled Molecular Electronic Switches in Nanoscale Metal–Molecule–Metal Junctions

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The transduction of a conformational change into electrical switching is an attractive approach to performing electronic operations with molecular building blocks. Although there are a few examples in the literature of conductance switching behavior in molecular junctions,^{1–3} the switching mechanisms are controversial and in some cases thought to originate from unexpected sources such as molecule–electrode bond fluctuations¹ or the reversible formation of metallic filaments through the molecular layers.² Photochromic molecules such as azobenzenes and diarylethenes are appealing candidate switches since they undergo well-characterized photoisomerizations.⁴ Very recently, electrical switching has been proved with these molecules using large-area contacts.^{3b,5,6} In this report, we consider conductance switching at the single domain level in nanoscale junctions consisting of azobenzene-based molecules⁴ which switch from an extended *trans* to a compact *cis* form upon UV irradiation.^{5,7}

Metal–molecule–metal junctions were produced by contacting a gold-supported self-assembled monolayer (SAM) with a metal-coated atomic force microscope (AFM) tip. AFM feedback electronics was used to maintain a constant, and minimally invasive, applied force of 2 nN. This conducting AFM (C-AFM) approach^{8–10} (Figure 1) has previously been applied to SAMs of molecules such as alkanethiols and oligophenylenes; however, this is the first time C-AFM has been employed to investigate molecular conductance switching due to an external stimulus.

The thiolated azobenzene (Azo) employed in this study (Figure 1) has been shown to form monocomponent well-ordered SAMs on Au(111) and, unlike azobenzenes bearing alkanethiol anchoring groups,¹¹ provides a surface packing which allows for efficient, and reversible, isomerization.^{5,7} In addition, the switching occurs over entire crystalline domains of tens of nanometers in size, making this system an ideal test-bed for investigation by C-AFM, which probes areas of 5–25 nm², depending on the tip radius used.

A marked increase in current was observed following UV irradiation, corresponding to the conformational change of the azobenzene molecules from *trans* to *cis* forms. Representative current–voltage (*I*–*V*) traces taken in the linear regime at low voltages (–0.3 to 0.3 V) are shown in Figure 2a. For each sample, a total of 300 to 800 *I*–*V* traces were recorded at 5 to 15 different locations, with the same tip, before and after UV irradiation. The resulting junction resistances, derived from linear fits of the *I*–*V* curves, were plotted in histograms. A log-scale of the resistance provided a normal distribution, suggesting that the variance in resistance has an exponential dependence, probably due to variations

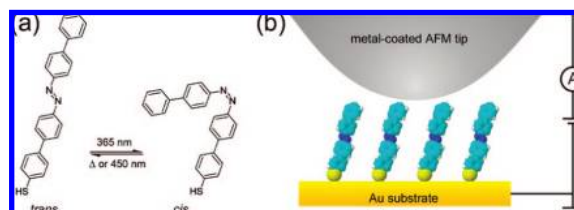


Figure 1 (a) Structure of the *trans* and *cis* isomers of the light-switchable azobenzene derivative considered in this study. (b) A schematic of the setup used for performing C-AFM measurements on azobenzene SAMs.

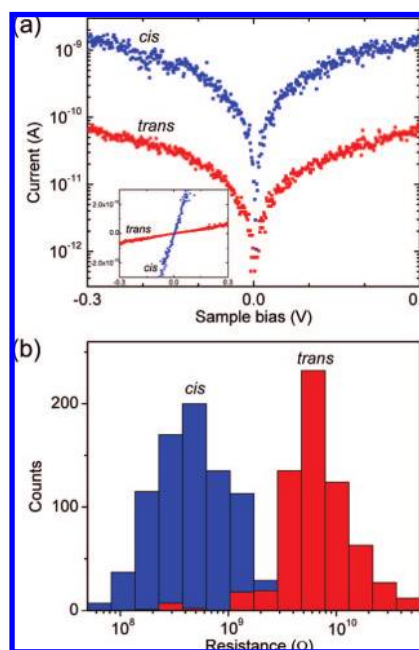


Figure 2 (a) Representative *I*–*V* traces (semilog scale) recorded before and after UV irradiation showing larger currents following photoisomerization into the *cis* conformation (linear scale in inset). (b) Resistance histogram (based on 1484 *I*–*V* curves) exhibiting distinct peaks corresponding to the *cis* and *trans* conformations of the Azo molecules.

in the tunneling length.¹² As shown in Figure 2b, two distinct resistance peaks are observed, with the higher resistance corresponding to the *trans* state and the lower corresponding to the *cis*. Analysis of 30 samples yielded a current switching ratio of about 30 between the *trans* and *cis* conformers. This behavior was similar for large radius (50 nm) Au-coated tips (15 samples), which gave a ratio of 29 ± 3, and small radius (20 nm) Pt–Ir-coated tips (15 samples), which gave a ratio of 27 ± 4.

Although conceptually very different in terms of type of measurement, this result is highly consistent with recent experiments

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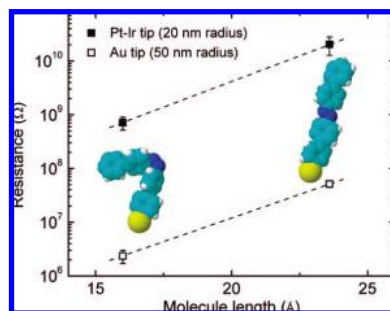


Figure 3. Semilog plot of resistance versus molecular length compiled from 15 sets of measurements with Au tips and 15 with Pt–Ir tips. The estimated β is represented by the slope of the dotted lines.

performed with a liquid Hg counter-electrode which showed a current switching ratio of about 25 in SAMs of the same molecule.⁵ This correspondence is not necessarily to be expected given not only the different chemical nature of the junctions used but also that the Hg drop experiment is a macroscopic measurement over a large ensemble of molecules, and the present C-AFM measurement involves ca. 90 molecules in the case of the 50 nm radius Au tips and 30 molecules for the 20 nm radius Pt–Ir tips. Owing to the macroscopic nature of the Hg drop experiment, the magnitude of the switching ratio may be diluted by the presence of some unswitched domains. In contrast, given that the isomerization has been revealed to produce crystalline domains of tens of nanometers,⁷ individual *cis* or *trans* domains are contacted in the C-AFM measurements (or small numbers thereof). This reduces the probability of measuring mixtures of *cis* and *trans* ensembles and is consistent with the slightly larger switching ratio obtained in the C-AFM measurements.

The decreased junction resistance in the *cis* state can be understood in terms of a reduction in the tunneling barrier length. Employing the equation typically used to describe nonresonant tunneling,^{8,9} $R = R_0 \exp(\beta s)$, the tunneling decay factor β can be estimated. Here, R is the measured resistance, R_0 is an effective contact resistance, and s is the tunneling distance. For a conjugated molecule, through-bond tunneling along the molecular backbone is expected to dominate over through-space tunneling. Therefore, the tunneling distance s is taken to be the length of the molecule. While the tunneling length for Azo molecules in the *trans* form corresponds to the full length from the Au–S linkage to the terminal H, the effective length of the *cis* isomer is only from the Au–S bond to the exposed azo group. Alternatively, because the molecular tilt angle may change in order to accommodate the bent *cis* structure, and in view of a possible rotation of the phenyl rings, it cannot be ruled out that contact with the AFM tip can also occur at the first carbon atoms above the azo group. In light of this, the length of the *trans* and *cis* isomers was estimated to be 23.6 and 16.0 ± 1.5 Å, respectively.

A summary of the junction resistances, plotted on semilog axes as a function of molecular length, is shown in Figure 3. According to the nonresonant tunneling equation, the slope represents β , which was determined to be $0.45 \pm 0.10 \text{ \AA}^{-1}$. This is in good agreement with the literature values commonly obtained for short conjugated molecules ($\beta = 0.4 - 0.5 \text{ \AA}^{-1}$).⁸ The uncertainty range was calculated based on the uncertainty in molecular length and resistance.

It should be kept in mind, however, that some assumptions are implicit in this estimate: First, since the molecular electronic structure is potentially modified by the *trans* to *cis* isomerization, β is not necessarily constant. Second, as described above, there is

some uncertainty with regard to the nature of the contact in the case of the *cis* isomer. It is expected that the effective contact resistance associated with the azo group and the phenyl rings would differ, as previous studies revealed significant differences in contact resistance depending on the molecular end group contacted by the electrodes.⁸ Despite these approximations, the behavior of azobenzene junctions is consistent with a simple variation in tunneling length. This may suggest that the electronic structure of the molecule, at least below the azo group, is not appreciably perturbed by the isomerization. Furthermore, this result favors the interpretation that the contact point of the molecule is a phenyl group in both conformations or that the azo and phenyl groups offer a similar contact resistance. The extent to which changes in electronic structure, molecular contact point, and dipole moment contribute to the junction resistance should be clarified through ab initio modeling. It should also be noted that there was a large difference in the magnitude of the resistance between the Au and Pt–Ir tips (ca. 2.5 orders of magnitude). Albeit the difference in contact areas accounts for some of this, it is likely that the difference in metal work function plays an important role, as well.¹³

In conclusion, we have quantitatively demonstrated by C-AFM the light-induced switching of the current in nanoscopic molecular junctions incorporating azobenzene-based molecules undergoing a *trans*–*cis* isomerization. A 30-fold decrease in resistance was found following transformation to the *cis* state. This is in line with the expected decrease in tunneling barrier length associated with the molecular conformational change.

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Supporting Information Available: Further details about sample preparation, experimental methods, and analysis. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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