

ELECTRONIC SUPPLEMENTARY INFORMATION (ESI)

Photoswitching electron transport properties of an azobenzene containing thiol-SAM

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Experimental Section Details

Chemicals 2-Phenylethanethiol (98%, Aldrich), ferrocenemethanol (97%, Aldrich) and LiCl (p.a., Riedel-de Haën) were used as received. Toluene (p.a., Riedel-de Haën), ethanol (94 w-%, Altia) and acetone (p.a., Lab-Scan) were used without further purification. Azobenzene derivatised thiol (AZO, see Figure S1) was obtained as a gift from Dr. Jerzy Paprotny. The water used was first distilled and then purified with a milli-Q® system.

The gold substrates used in the experiments were commercial gold-coated borosilicate glass substrates (Gold Arrandee™). The gold surface was flame annealed in a Bunsen burner prior to use according to the instructions of the manufacturer to form an Au(111) surface¹. Before annealing, the substrates were rinsed with 99 % ethanol and dried in a nitrogen stream.

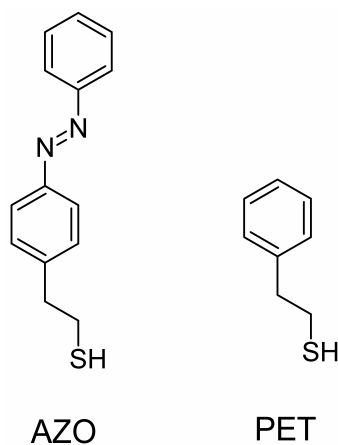


Figure S1. Thiols used in the experiments.

Formation of the self assembled monolayers Thiols were assembled at the surface by immersing for ~ 3 days the substrates into a 2.5 mM AZO toluene solutions containing different concentrations of PET so that the mol fraction of AZO in the solution was 1, 0.8, 0.6, 0.4 and 0.2. The samples were kept in dark during the immersion. A SAM containing only PET was also prepared in a similar way using a 37 mM solution of PET in toluene. Prior to SAM formation, the samples were rinsed with ethanol and dried in a nitrogen stream. After the formation of the monolayer, the samples were kept immersed in pure toluene for 10 minutes to ensure the removal of unbound thiols. After rinsing with copious amounts of toluene the samples were finally dried in a nitrogen stream.

SECM measurements SECM experiments were performed to study the change in the rate of electron transfer reaction through the SAMs brought about by the photoisomerisation of AZO. To maintain AZO in a chosen conformation, the measurements were carried out under constant light irradiation. Wavelength of 436 nm was used to keep the AZO as the *trans* isomer and 366 nm for the *cis* isomer. The light source was a 300 W Xe-lamp (Oriel 6259) and the wavelength was controlled with a monochromator (Oriel MS257) and its output was launched in an optical cable leading the light to the sample.

Approach curves were recorded for the SAMs in both its *trans* and *cis* isomers. The measurements were carried out using a commercial 10 μm Pt tip (CH Instruments) and Ag/AgCl wire as the quasi reference electrode. Approach curves were measured in aqueous solution using 1 mM ferrocenemethanol as the mediator and 0.1 M LiCl as the supporting electrolyte. The Pt tip was polished and shaped with 0.3 μm alumina and rinsed with milli-Q water and acetone prior to every set of measurements. The *RG* value of the tip was ~ 5. Using 0.25 V tip potential, 15-25 approach curves were recorded at an approach rate of 1 $\mu\text{m/s}$ for each sample. The position of the tip was changed after each measurement to ensure a representative set of data.

For each measurement, a value for k_{ET}/D was determined by fitting a theoretical tip current to the measured data. The electron transfer rate constant and its standard deviation were found by fitting a Gaussian function to the set of data measured from each sample. Example of measured approach curve for a sample containing 20 % AZO in the *trans* conformation is shown in Figure S2a. The corresponding distribution of k_{ET}/D values and the Gaussian function fitted to them is shown in Figure S2b.

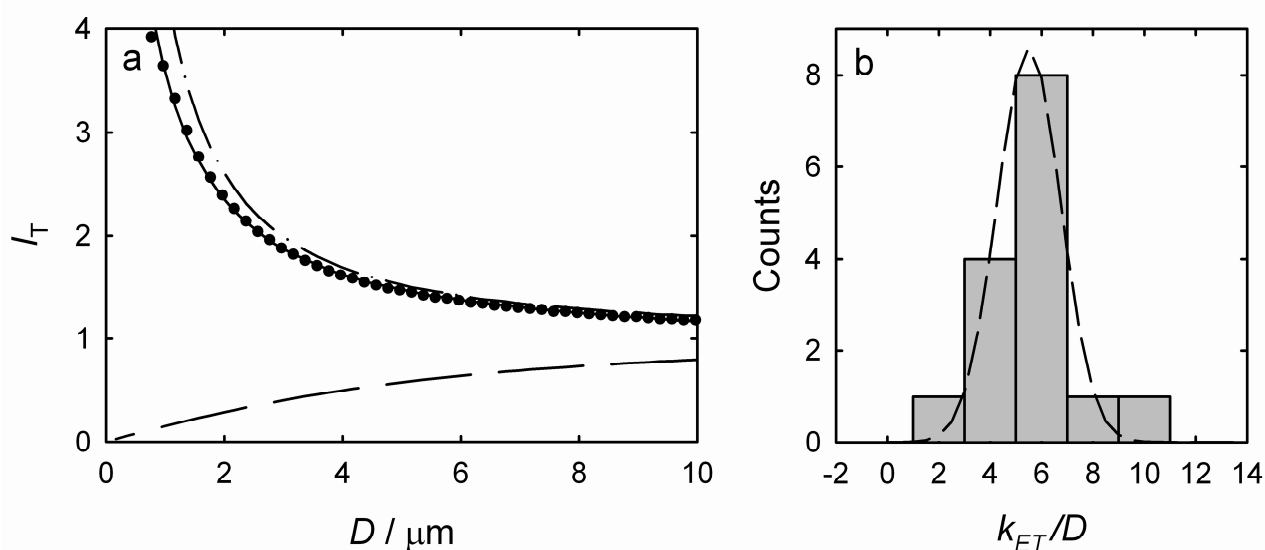


Figure S2. (a): Measured approach curve (black dots) and theoretical tip current (solid line) for the sample containing 20 % AZO in *trans* conformation. The ideal positive feedback (dashed line) and negative feedback (dash-dot line) are shown for comparison. (b): Distribution of k_{ET}/D values extracted from the fitting of tip currents. The value of Λ was obtained from a fitted Gaussian function (dashed line).

Ellipsometry Variable angle laser (632.8 nm) ellipsometry (Picometer Ellipsometer, Beaglehole Instruments) was used to determine the thicknesses of both the *trans* and the *cis* SAMs. Before the measurements of the *cis* SAMs, the samples were photoisomerized with 366 nm UV light keeping them under the same optical set up as in the SECM measurements for 15 minutes. The data was collected in 0.5 degree intervals from 65 to 80 degrees using a time constant of 0.1 s. To gain the highest sensitivity, the angles were chosen around the Brewster angle of gold ($\sim 74^\circ$). All the measurements were performed in a dark room to prevent unwanted isomerization of the SAM.

AFM AFM (Nanoscope III) in Tapping mode was employed to study the topography of the gold substrates. Single crystal Si tip with resonance frequency 200-400 kHz was used. In Figure S3, an image obtained from a bare gold substrate is shown. The grain size of the Au(111) domains varied between 1 and 10 μm^2 .

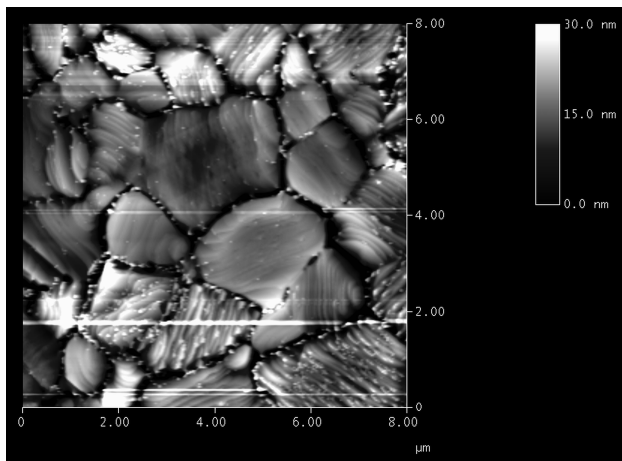


Figure S3. An AFM image of a bare gold substrate.

References

- (1) Anon. How to use. http://www.arrandee.com/Products/How_to_use/body_how_to_use.html (accessed 2/26, 2007).