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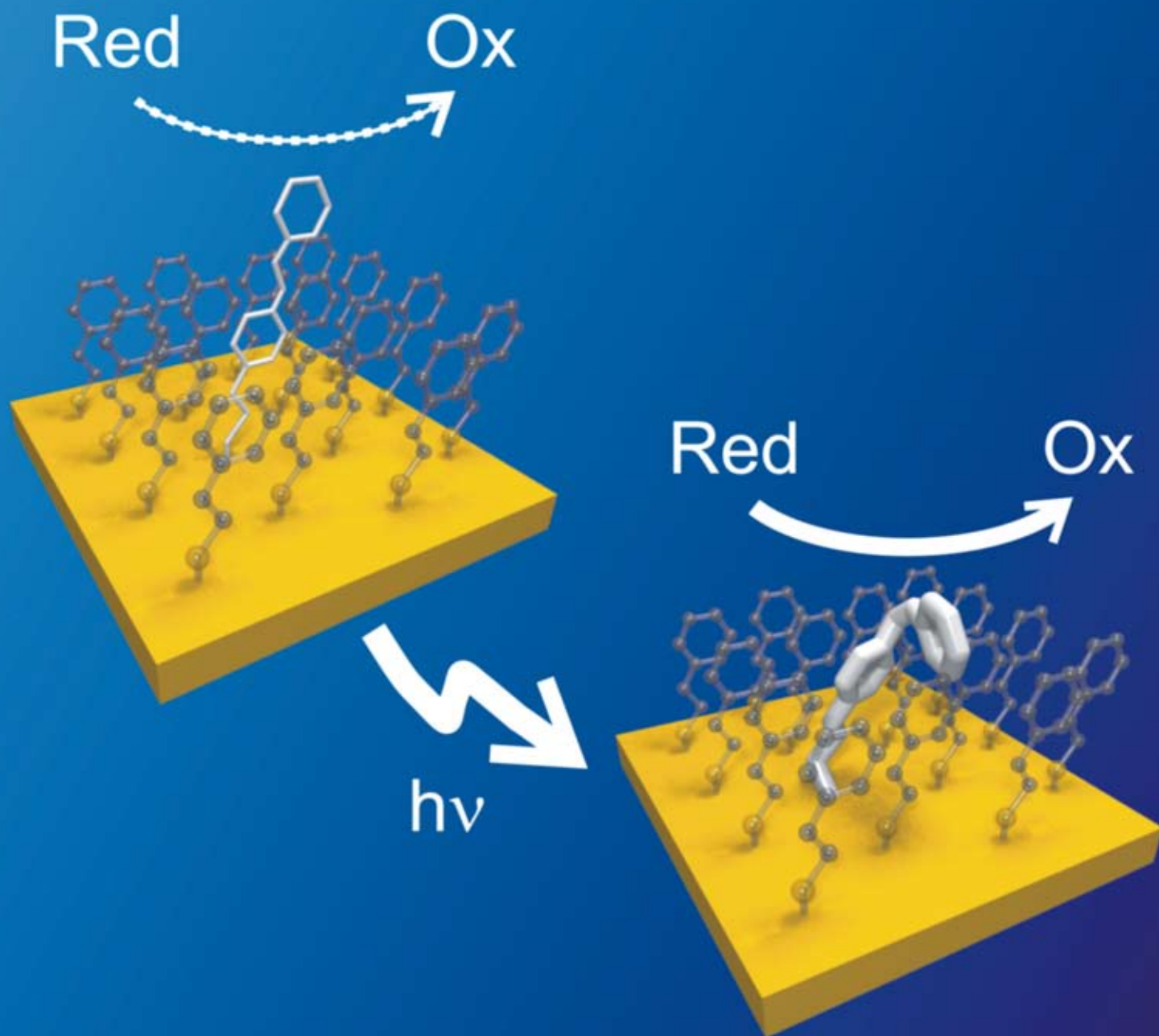
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Photoswitching electron transport properties of an azobenzene containing thiol-SAM†

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The influence of conformational and electrical properties of azobenzene molecules on the electron transfer barrier properties of their SAMs was studied by SECM and ellipsometry.

Molecular wires are an important field of research as potential components in molecular electronics circuits and the understanding of electron transfer through them plays an important role in nano-scale research. Controlling the electrical properties of molecular wires is essential when designing devices at the molecular level. Several types of molecular switches, including those based on changes in conformation or conductance,^{1,2} have been recently described. Azobenzene compounds have gained much attention because of the ability to control both conformation^{3,4} and conductance⁵ of the molecule by photoisomerisation. Light energy is transformed to mechanical work in the photoisomerisation process of the azobenzene group.⁶

Spontaneous formation of self-assembled monolayers (SAM) has been utilised in the determination of molecular conductance of thiol terminated molecules. SAMs have been studied widely with both conventional electrochemistry^{7–9} and scanning electrochemical microscopy (SECM).^{10–12} Previous studies have considered the conductance of both saturated and unsaturated thiolates, but thiols containing redox centers have also been investigated.^{10,13–15} Studies of molecular conductance rely on assumptions regarding molecular conformation. In the present work, by contrast, the real effective thicknesses of SAMs, *i.e.*, the electron tunnelling distance, has been measured by ellipsometry.

SECM has been previously employed for studying electron¹⁶ and ion¹⁷ transfer in thin polymer films. In this work, the barrier properties of a SAM constructed from an azobenzene thiol (AZO) and 2-phenylethylthiol (PET) as a spacer (Fig. 1) were studied by SECM. The effect of the conformation of AZO in the SAM was analysed by determining the decay constant β ($\beta = -d \ln k_{ET}/dr$, where k_{ET} = the apparent heterogeneous rate constant of electron transfer and r = the

thickness of the layer) for monolayers constructed with both AZO isomers and PET in different molar ratios. β was determined by measuring k_{ET} through the layer as a function of layer thickness. This work shows the ability of SECM to probe changes at a molecular level through measurement of macroscopic properties.

Thiols were assembled on a Au(111) surface by immersing the substrates into toluene solutions while varying the AZO/PET concentration ratio so that the AZO content of the solution was 100, 80, 60, 40, 20 and 0% (pure PET). During immersion, the solutions were kept in the dark and, therefore, AZO was present in the SAM in the more stable *trans* conformation.

The rate of electron transfer through the SAMs and the changes brought about by photoisomerisation were measured by SECM.^{10,11} To maintain AZO as a particular isomer, the measurements were carried out under constant irradiation of light. A wavelength of 436 nm was used to keep the AZO molecule as the *trans* isomer and at 366 nm as the *cis* isomer. The SECM measurements were carried out using a 10 μm Pt tip (CH Instruments) and a Ag/AgCl wire as a quasi reference electrode. Approach curves were measured in aqueous solution using 1 mM ferrocenemethanol (FcMeOH) as the mediator and 0.1 M LiCl as the supporting electrolyte. The RG value of the tip was ~ 5 ($RG = r_g/a$; r_g = radius of the tip and a = radius of the Pt-wire). Using a tip potential of 0.25 V, 15–25 approach curves were recorded at an approach rate of 1 $\mu\text{m s}^{-1}$ for each sample. The position of the tip on the surface was changed after each measurement to ensure a representative set of data. For each measurement, a Gaussian function was fitted to the set of data and the resulting expectation value was used as the final result with the standard deviation as the error estimate (see ESI for details†).

The effective apparent rate constant k_{eff}^{10} for the electron transfer reaction between the mediator and the substrate was determined by fitting the normalised measured data to the combination of theoretical approach curves for pure positive

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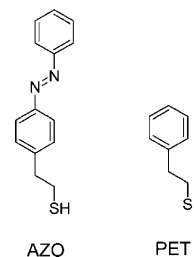


Fig. 1 Thiols used in the experiments.

and negative feedback. Non-linear regression analysis was used to fit the experimental results to the dimensionless kinetic parameter Λ ($\Lambda = k_{\text{eff}}d/D$, where D = the diffusion coefficient of the mediator, $7.0 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ and d = the tip-substrate separation). The normalised tip current (I_{T}^k) as a function of the dimensionless tip-substrate separation ($L = d/a$) within the range $0.1 \leq L \leq 1$, is given by:¹⁸

$$I_{\text{T}}^k = \left[\frac{0.78377}{L(1 + \frac{1}{\Lambda})} + \frac{0.68 + 0.3315 \exp(\frac{-1.0672}{L})}{1 + F(L, \Lambda)} \right] \times \left(1 - \frac{I_{\text{T}}^{\text{ins}}}{I_{\text{T}}^{\text{c}}} \right) + I_{\text{T}}^{\text{ins}} \quad (1)$$

where the dimensionless tip current for an ideal insulator, $I_{\text{T}}^{\text{ins}}$ and an ideal conductor, I_{T}^{c} , for an electrode having $RG = 5$ are:^{19,20}

$$I_{\text{T}}^{\text{ins}} = \frac{1}{(0.48678 + \frac{1.17706}{L} + 0.51241 \exp(\frac{-2.07873}{L}))} \quad (2)$$

and

$$I_{\text{T}}^{\text{c}} = 0.72035 + \frac{0.75128}{L} + 0.26651 \exp\left(\frac{-1.62091}{L}\right) \quad (3)$$

where

$$F(L, \Lambda) = (11 + 7.3\Lambda)/(\Lambda(110 - 40L)) \quad (4)$$

The measured current was made dimensionless by dividing it by the theoretical steady-state current far away from the surface, I_{lim} , ($I_{\text{lim}} = 4nFDC^b a$, where n = the number of electrons transferred per electroactive molecule, F = the Faraday constant and C^b = the bulk concentration of the mediator).

Typical approach curves are given in Fig. S2a† and the corresponding distribution of Λ values and the Gaussian function fitted to them is shown in Fig. S2b. The measured currents showed a clear positive feedback and the values for the apparent effective rate constant, k_{eff} , varied between 0.11 and 0.39 cm s^{-1} . Since the monolayer does not include any electrochemically active sites, the measured apparent rate constant k_{eff} corresponds to the rate constant of electron transfer (k_{ET}) across the SAMs.¹⁰ The values for k_{ET} reported above are larger than those measured for monolayers of alkanethiols.¹⁰ The main reason for the larger rates of electron transfer is the high degree of conjugation of the AZO and PET thiols. The possible formation of separate thiol phases in the mixed monolayers and the penetration of the redox mediator into the SAM may also affect the values of k_{ET} (see Fig. 2 and discussion below).

Heterogeneous rate constants measured for both isomers are shown in Fig. 2a. A clear decrease of k_{ET} with increasing surface mol fraction of AZO is observed implying that the electron tunnelling distance increases with the amount of AZO in the SAM. The differences between the rate constants of the *trans* and *cis* SAMs are presented in Fig. 2b. The general trend is that the electron transfer rate is higher for the thinner *cis* SAMs than for the thicker *trans* SAMs. The free space in the SAM increases as the relative concentration of the spacer molecules is increased. Increasing the molar fraction of PET makes the effect of isomerisation in thickness more pronounced. This is observed in Fig. 2b as an increased difference in the electron

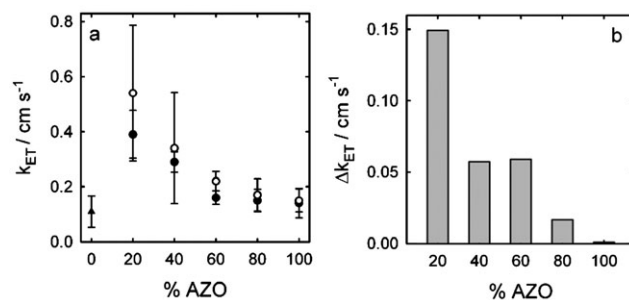


Fig. 2 (a): Electron transfer rate constants measured through the *trans* SAM (black dots), the *cis* SAM (circles) and PET (black triangle). The error bars represent the standard deviation of the apparent rate constants. (b): Differences between the rate constants for *trans* and *cis* SAMs.

transfer barrier of the different isomers as the fraction of PET is increased.

The resulting k_{ET} of samples containing pure AZO (100%) and pure PET (0%) give an insight to the structure of the monolayers (Fig. 2). Although being shorter, PET hinders electron transfer rate more effectively than AZO indicating a tighter molecular packing in the PET monolayer. The lower density of the AZO layer may enable the redox carrier employed, ferrocenemethanol, to permeate into the SAM thus resulting in an increased rate of electron transfer across the SAM.

The standard deviation of k_{ET} is nearly constant throughout the whole series of SAMs apart from the samples containing 20 and 40% AZO. These samples clearly show higher deviation in k_{ET} , compared to the other mixed monolayers. This indicates a low ordered packing or more likely the formation of separate thiol phases in these SAMs, which is not as apparent for the other concentrations studied. Permeation of ferrocenemethanol into these layers can also be considered more likely.

Variable angle 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 photoisomerised with 366 nm UV light. *Trans* samples were not irradiated prior to measurements. To gain the highest sensitivity, the measurement angles were chosen around the Brewster angle of gold ($\sim 74^\circ$).

The thickness of the SAMs was determined by fitting the ellipsometry data to a two-layer model. The optical constants for a bare gold substrate were measured and used as the substrate properties. The SAM was modelled as a dielectric material with a refractive index of 1.6. This was selected near the values for the bulk compounds, 1.604 for AZO and 1.554 for PET, estimated using a chemistry modelling software.²¹ The resulting thicknesses calculated were $\sim 6 \text{ \AA}$, higher than those predicted by molecular modelling.²¹ This may be due to the presence of a thin water layer adsorbed from air during the irradiation of the sample or most likely, to changes of the dielectric function of the gold film on chemical functionalisation. The assumptions within the model used may cause some uncertainties in the results, but on the other hand, a more complex model involving, for instance, changes in the dielectric function for the gold surface, would have an unrealistic large

Table 1 Effective thicknesses of the SAMs measured by ellipsometry

% AZO	<i>trans</i> Thickness/Å	<i>cis</i> Thickness/Å
0	12.5 ± 1.2	12.5 ± 1.2
20	14.5 ± 2.9	12.1 ± 3.5
40	14.2 ± 1.5	10.6 ± 1.1
60	16.5 ± 0.5	12.8 ± 1.5
80	23.2 ± 0.6	16.2 ± 0.2
100	21.3 ± 0.4	18.8 ± 2.1

number of adjustable parameters. It has been shown in the literature that there is a measurable difference in the refractive index of the different isomers of azobenzene compounds.²² However, this difference was neglected in this study since the effect of photoisomerisation was more pronounced in the thicknesses of the SAMs than in the refractive index and the separation of these two variables is not possible when using angle resolved ellipsometry.

The results of the ellipsometry measurements are presented in Table 1. The errors obtained from the fitting of the measured data are used as the error estimates of the thicknesses. The thicknesses of the samples containing AZO are shown in Fig. 3a. The sample containing pure PET has been left out from this analysis because of the above mentioned different packing density of the molecules, which is likely to have an effect on the whole character of the monolayer. The difference in the length between the *trans* and *cis* isomer SAMs for the 100% AZO film is 2.5 Å, in agreement with the value of 2.5 Å determined by Monti *et al.*²³ Thus, differences in thickness can be measured with good accuracy by ellipsometry for these SAMs, allowing a good estimate of the decay constant for electron transfer (β).

The dependence of the logarithm of k_{eff} across the SAMs on effective layer thickness is shown in Fig. 3b. The thickness was calculated using the result of linear regression from Fig. 3a. From the slopes in Fig. 3b, β was 0.12 Å⁻¹ for the *trans* SAM and 0.17 Å⁻¹ for the *cis* SAM. The lower value of β for *trans* SAM implies a higher conductance through the monolayer. The values of β are typically 1 Å⁻¹ for the alkanes¹² and lower for unsaturated molecules.^{14,15,24,25} One possible reason for the observed increase of the decay constant is the decrease of

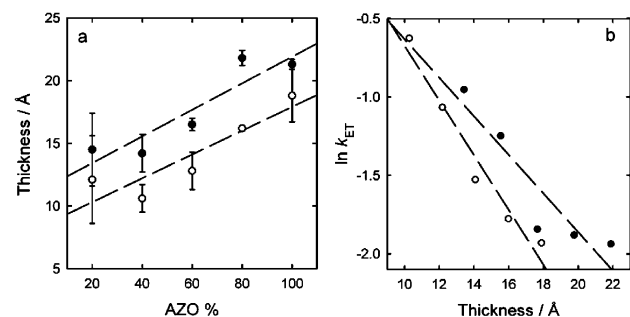


Fig. 3 (a) The measured thicknesses of the SAMs as a function of the molar fraction of AZO. The lines are linear fits to the measured data. (b) Dependence of the logarithm of the rate constant for electron transfer on the thickness of the SAM for the *trans* (black dots) and *cis* (white dots) conformers of AZO. The thickness scale has been calculated from the linear regression of the results in Fig. 3a.

conductance of the azobenzene group due to isomerisation, as predicted and measured by Zhang *et al.*^{3,5} This observation can be rationalised in terms of the molecular electronic structure of the isomers. The conductance of *cis* AZO is lower due to the loss of molecular orbital symmetry on isomerisation.²⁴ Another explanation for the differing barrier properties of the two isomers is the difference in the permeation rates of the redox mediator through the monolayers discussed by Walter *et al.*⁴ In addition, the decay constant obtained is measured for a mixed monolayer and with a lateral resolution lower than the dimensions of the surface domains supporting the SAMs (the diameter of the Pt-tip 10 μm compared with that of the Au(111) domains of less than 2 μm, see Fig. S3 in the ESI†). Thus, the decay constant measured is a value averaged over the whole array of molecules in the SAM. The permeation of FcMeOH into the SAMs could additionally lower the value of β but in spite of these uncertainties, the effect of isomerisation is clearly visible from the results presented.

The importance of this work is to demonstrate that photoisomerisation leads to measurable changes in the barrier properties of AZO–PET mixed monolayers. The composition of the SAM determines both the effective thickness and the extent of isomerisation of the SAM. It is shown that the electron transfer rate constant decreases exponentially as a function of the effective thickness for both *trans* and *cis* SAMs and from this dependence, the decay constants β of the SAMs have been determined. It is shown that it is possible to measure the effect of photoisomerisation on the conductance of a SAM containing azobenzene-terminated thiols employing SECM. Combining SECM with ellipsometry allows the estimation of the influence of both the layer thickness and conformation of the molecules on the barrier properties of their SAMs.

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