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Highly Efficient Photoswitch in Diarylethene-Based Molecular Junctions

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Supporting Information Placeholder

ABSTRACT: Thin layers of diarylethene oligomers (oligo(DAE)) were deposited by electrochemical reduction of a diazonium salt on glassy carbon and gold electrodes. The layers were fully characterized using electrochemistry, XPS, and AFM, and switching between open and closed forms using light was evidenced. Solid-state molecular junctions (MJs), in which a C-AFM tip is used as the top contact, were fabricated with total layer thicknesses fixed at 2-3 nm and 8-9 nm, i.e. below and above the direct tunneling limit. DAE was then photoswitched between its open and closed forms. Oligo(DAE) MJs using the open form of DAE are highly resistive while those with DAE in the closed form are more conductive. ON/OFF ratios of 2-3 and 200-400 were obtained for 3 nm- and 9 nm-thick DAE MJs, respectively.

Nanoelectronics is based on switching devices, and molecular electronics have tried to use various active molecules to develop resistive switches. Some approaches are based on redox-active molecules¹⁻⁹ while others are based on photoactive systems,¹⁰⁻¹⁷ with few studies combining the two properties.¹⁸⁻²² In this context photochromic molecules, i.e. molecules with two different forms (open/non-conjugated and closed/conjugated), which can be interconverted by light irradiation, have been widely used and incorporated into single-molecule and large-area Molecular Junctions (MJs).^{23,24} Most studies are devoted to monolayers or single-molecule-based MJs where the dominant transport mechanism is direct tunneling. In these systems the reported ON/OFF ratio or reversibility is not as good as expected. Gold electrodes quench the excited state of the molecules and prevents reversibility.²⁵⁻²⁷ In other studies, ON/OFF ratios are mostly below 100^{13,14,28,29} and it is only recently that a high ON/OFF ratio³⁰ with good reversibility was reported, using a strategy that decouples the active unit from the electrode.³¹ MJs incorporating photochrome-based layers about 5 nm-thick show reversibility but the ON/OFF ratios are disappointingly below 10 despite the fact that the main transport regime is hopping³² and allows a stronger molecular signature on transport.³³⁻³⁷

In this work, we prepare MJs using molecular layers based on photochromic diarylethene oligomers, grafted by diazonium salt electroreduction, and compare ON/OFF ratios for two different layer thicknesses corresponding to different transport regimes. It is found that both layers can be reversibly switched and that low ON/OFF ratios (2-3) are

observed in the direct tunneling regime while ON/OFF ratios above 200 can be reproducibly obtained in the hopping regime.

Perfluoro-1,2-bis(2-(4-aminophenyl)-5-methylthien-4-yl)-cyclopentene was synthesized by a known procedure²⁶ (Figure 1a). This molecule incorporates a photochromic core and bears two aniline groups (DAE-(C₆H₄NH₂)₂). In solution, as expected, photocyclization requires UV light (365 nm), and photoreversion occurs with visible light (435 nm) (see SI files Figure S1). The aniline groups were used for in situ diazonium generation and layer deposition (Figure 1b).³⁸⁻⁴² Such layers, referred to as oligo(DAE)_{xnm}, where x is the thickness in nm, were grafted onto a bare gold electrode and a C-AFM (Conducting-Atomic Force Microscopy) tip was used as the top electrode to complete the MJ (Figure 1c).

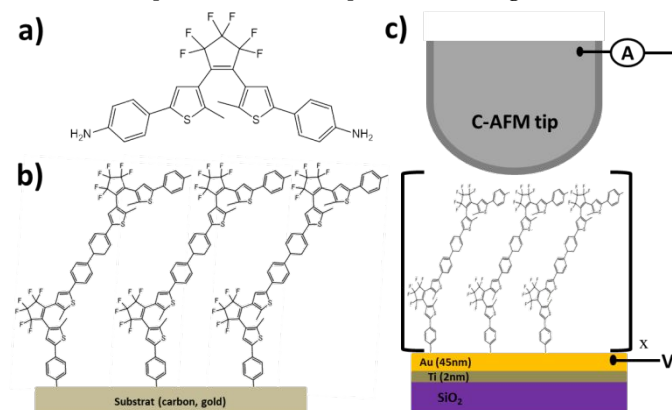


Figure 1. Schematic illustration of: (a) DAE-(C₆H₄NH₂)₂. (b) Idealized layer obtained after electroreduction of the corresponding diazonium salt. Note that the DAE units in the layer are not as organized as depicted in this ideal representation (c) SiO₂/Ti_{2nm}/Au_{45nm}/oligo(DAE)_{xnm}/C-AFM tip (Pt_{25nm}/Ir_{5nm}) molecular junction; x is the layer thickness.

The electrochemical behavior of DAE-(C₆H₄NH₂)₂ was investigated by cyclic voltammetry (CV). Glassy carbon (GC) electrodes were immersed in an acetonitrile (ACN) solution containing 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) as supporting electrolyte and 0.5 mM of DAE-(C₆H₄NH₂)₂ in its open or closed form (after irradiation of the solution). Figure 2a shows the CV in the positive potential range. For the open form, it displays one irreversible redox signal at 0.81 V/SCE which can be attributed to the oxidation of the aromatic amine (black). The CV of the closed form shows two peaks, one reversible at

0.47 V/SCE and a second, weaker, irreversible peak at 0.87 V/SCE (green). The first peak is associated with the oxidation of the closed DAE core and the second is related to the oxidation of the amine unit. These results are similar to those reported in the literature and indicate that the HOMO of the closed form of DAE is close to -5.6 eV while that of the open form is much lower as calculated previously.³⁰

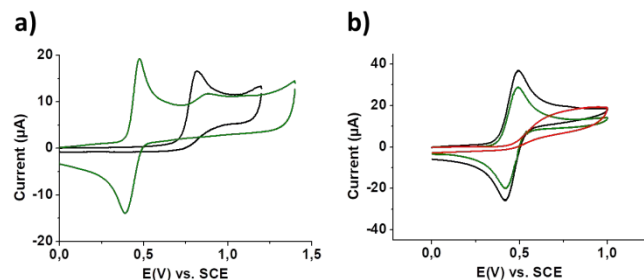


Figure 2. (a) CVs of DAE-(C₆H₄NH₂)₂ (black) open and (green) closed form in oxidation range. (b) Ferrocene electrochemical responses (5 mM solution in ACN) on bare (black) and diarylethene-modified carbon electrodes before (red) and after (green) UV irradiation. Supporting electrolyte: 0.1 M TBAPF₆; scan rate 0.1 V.s⁻¹, 16 CV scans were used for grafting oligo(DAE)

Then we grafted DAE-(C₆H₄NH₂)₂ onto GC or gold electrodes, generating the diazonium salt in situ by adding 10 equivalents of tBuONO. Details on the electrochemical conditions are given in Figure S2 which shows the CV of the reduction of the diazonium salt of DAE in the open form. It displays, on carbon, an irreversible cathodic wave centered at -0.13 V/SCE, attributed to the reduction of the diazonium cation. During subsequent cycles, it progressively decreases. A similar behavior is observed on gold electrode (Figure S2b). This behavior is common for the electroreduction of diazonium salts and indicates that an insulating organic layer has been deposited on the substrate. The electroactivity of the DAE-modified electrode was studied in the presence of ferrocene or decamethylferrocene redox probes before and after UV irradiation (see SI files for irradiation conditions). Compared to the bare electrode (Figure 2b, black), the CV of ferrocene (Figure 2b, red) and decamethylferrocene (Figure S3, red) on the DAE-open (DAE-o)-modified electrode does not show a reversible signal at the potential where they are usually oxidized. The layer formed on the electrode prevents the oxidation of the probe and the probe signals are partially blocked, with irreversible signal characterized by a ΔE_p above 600 mV. After UV irradiation, ferrocene and decamethylferrocene show reversible signals (Figure 2b, green and Figure S3 green) very close to that observed on a bare electrode (reversible signal with ΔE_p close to 60 mV). This indicates that some closed DAE units (DAE-c) have been generated on the surface by irradiation. Such units can act as electron relays and generate pinholes or nanopores in the initial layer, allowing ferrocene and decamethylferrocene to be reversibly oxidized. The number of DAE units undergoing this switch is unknown but the number of nanopores is high enough for the layer to become partially transparent towards ferrocene and decamethylferrocene. Note also that when the layer is further irradiated using visible light, decamethylferrocene signal is blocked showing that the photoswitch is reversible (see Figure S3 red, dash dotted).

To characterize the layers by X-ray photoelectron spectroscopy (XPS), gold electrodes were modified by oligo(DAE) (Figures 3a, b and c). Peaks corresponding to fluorine, carbon, gold and sulfur are seen (Figure 3a). The gold peaks are still observable, suggesting that the layer is less than 10 nm-thick. The high-resolution spectrum of S2p shows the typical double peaks S2p_{1/2} and S2p_{3/2} at 164.6 eV and 165.2 eV attributed to the sulfur of the thiophene rings (Figure 3b). The high-resolution spectrum of F1s displays a peak at 688.6 eV which corresponds to fluorine atoms of the DAE (Figure 3c). The high resolution spectrum of C1s (Figure S4a) shows two main peaks at 285 eV and 290 eV attributed to aromatic carbon atoms and carbon atoms bonded to fluorine while the small N1s peak at 400 eV (Figure S4b) confirm that no azo groups are detected in the film and that some unreacted amino group may be involved as terminal groups of the layer. The atomic ratios obtained from the experimental XPS data and the theory of the oligo(DAE) single layer are presented in Figure 3d. The calculated fluorine/sulfur ratio (F/S) is about 3.2 and the expected value is 3. The experimental (C/S) and (C/F) ratios are about 15 and 4.6, also in good agreement with the theoretical values of 13.5 and 4.5, respectively. These results further confirm that layers of oligo(DAE) are easily formed on gold by diazonium electroreduction.

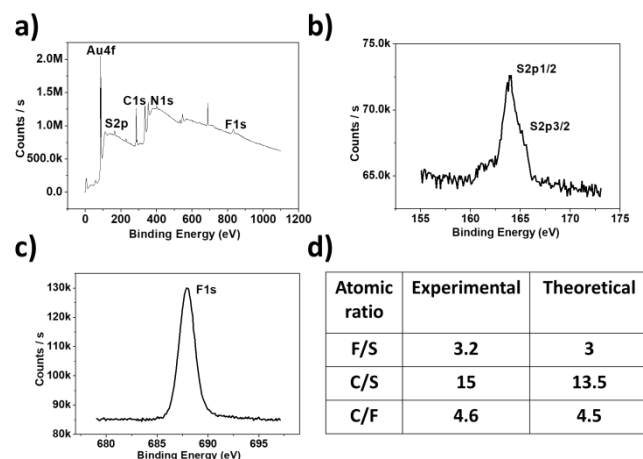


Figure 3. Characterization of oligo(DAE)-modified gold surface (layer thickness 8 nm):. (a) survey XPS. (b) High-resolution S2p XPS spectrum. (c) High-resolution F1s XPS spectrum. (d) Atomic ratio calculated from experimental data and theory. C1s and N1s spectrum are given in SI files

We then grafted this molecule onto gold micro-electrode stripes (20 μm x 2 cm and 45 nm-thick on Ti/SiO₂). Different layer thicknesses were generated and measured by AFM making scratches in the layer or measuring the cross-sections of the modified and bare gold stripes. The thickness of the layer, deposited on gold, can be controlled by changing the deposition conditions (Table S1). In the following, layers with total thickness around 3 nm and 9 nm were used. Figure S5 shows one example of AFM statistical analysis in which we measured a thickness of 46 nm, and 49.1 nm for the bare and the DAE-modified electrodes, respectively. An average thickness of 3.1 nm is found. Other DAE-modified electrodes with an average thickness of 8.6 nm were also fabricated (Figure S6). The roughness of the layers was estimated to be around 1 nm, which is close to the value for bare gold, ca. 0.8 (Figure S7).

Overall these results indicate that ultrathin DAE layers can be easily deposited on various surfaces (GC and gold) by diazonium salt electroreduction. Moreover, the DAE layers grafted on carbon electrodes photoswitch despite being in the solid state, and the thickness of the layer can be easily varied by changing the deposition conditions (Details are given in Table S1).

A C-AFM tip was used as top electrode to complete an MJ and to investigate the transport properties of both thin (3 nm) and thick (9 nm) diarylethene-based layers in the two photostationary states called OFF (non-irradiated layers, DAE-o) and ON (irradiated layers, DAE-c). Figure 4 displays the *IV* characteristics of the two MJJs (more data are given in Figure S5). For both junctions, the measurements were first performed with layers deposited from a solution containing DAE in its open form (the two thiophenes are electrically disconnected; therefore, this corresponds to the OFF state). Then both junctions were switched to the ON state using UV irradiation at 365 nm, and the *IV* characteristics were determined again. By visible light irradiation at 435 nm both junctions were switched back to the initial state and the measurements were repeated to test reversibility. For each junction, 200 to 500 *IV* traces were recorded at 5 to 15 different locations before and after irradiation.

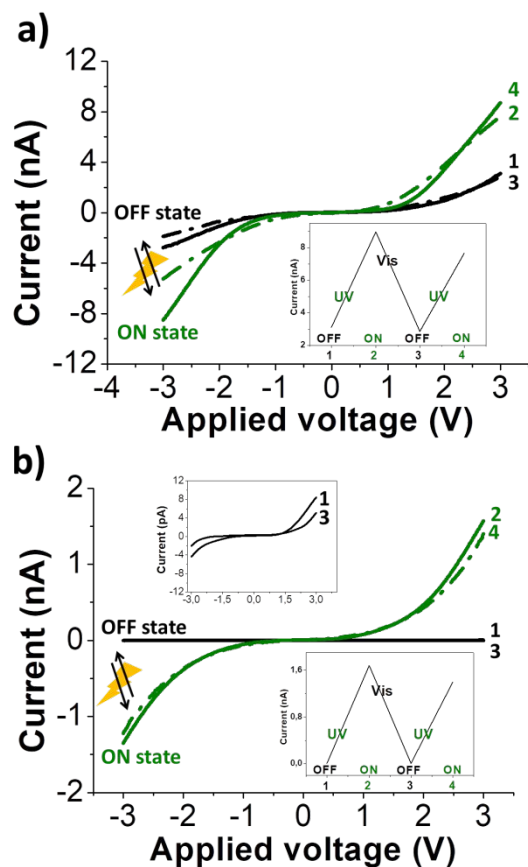


Figure 4. *IV* characteristics (black) before and (green) after UV irradiation of: (a) DAE_{3nm}; (b) DAE_{9nm} junctions measured by C-AFM at 3 V. Upper inset shows the zoom of the black curves in (b). Lower insets show the reversibility cycles for the corresponding curves.

Figure 4a compares the average *IV* curves of the DAE_{3nm} MJJs before (black) and after (green) UV irradiation. These curves show that the current depends on the isomerization state of the layer. The current reaches 3 nA at 3 V when the photochromic units are in their open form (curve #1) while

that measured when the layer has been UV irradiated increases to about 8.5 nA at 3V (curve #2) and returns to its original value after irradiation with visible light (curve #3). This process is reversible, as depicted in the inset of Figure 4a. The MJ can be switched reversibly between a high and a low resistive state with an ON/OFF ratio of 3. For a single-molecule junction, a theoretical ON/OFF ratio above 10⁴ can be calculated, if we assume an attenuation factor of 9 nm⁻¹ for the open form (non-conjugated system) and of 3 nm⁻¹ for the closed form (conjugated system), if transport occurs by direct tunneling, where $J = J_0 \exp(-\beta d)$, and d is the layer thickness.³³⁻³⁴ Only a few examples have been reported with ON/OFF ratios above 10 in this transport regime²⁵⁻³¹. In the present case the small ON/OFF ratio is in line with many previous results^{3,14,28,29,32} and can be attributed to partial quenching of the isomerization by the electrodes, by incomplete photoisomerization, which always occurs in multiphotochromic systems⁴³, and by the fact that in the direct tunneling regime a small molecular signature on transport is observed in the strong coupling regime.³³⁻³⁷

Figure 4b shows the average *IV* curves of the DAE_{9nm} MJ before (black) and after (green) UV irradiation. Figure S19 shows the same data in logJ versus V format for direct visualization of the ON/OFF ratio. These curves show that the current now strongly depends on the isomerization state of the layer and that in the OFF state it is much smaller than in the DAE_{3nm} MJ (see upper inset in Figure 4b and Figure S19). The current is only 5 to 8 pA at 3 V when the layer consists of DAE oligomers mainly in their open form, while it reaches 1.6 to 1.8 nA at 3 V when the layer has been UV-irradiated. Again, the current returns to its original value after irradiation with visible light and the switch is reversible. An exciting result is that ON/OFF ratios between 200 and 400 are obtained thanks to the highly resistive behavior of the DAE_{9nm} MJ in its OFF state, where most of the DAE units are in their open form. Comparing the observed currents for DAE_{9nm} and DAE_{3nm} MJJs and assuming $J = J_0 \exp(-\beta d)$ leads to effective attenuation factors of 1 nm⁻¹ and 0.23 nm⁻¹ for the ON and OFF photostationary states, respectively. These values are significantly lower than those for direct tunneling, and clearly demonstrate that hopping is the dominant transport mechanism in DAE_{9nm} MJJs. ON/OFF ratios of 200-400 clearly indicate a strong molecular signature on transport and show that it is maximized when the layer thickness is above 5 nm and hopping prevails.

Thin layers of DAE oligomers have been deposited by electrochemical reduction of a diazonium salt on GC and gold electrodes. Switching between two different photostationary states using light was evidenced for modified electrodes and solid-state MJJs. MJJs with DAE layer thicknesses of 2-3 nm and 8-9 nm, i.e. below and above the direct tunneling limit, are very different and exhibit ON/OFF ratios of 2-3 and 200-400, respectively.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website. It includes UV-Vis, electrochemical deposition, AFM and *IV* curve analysis.

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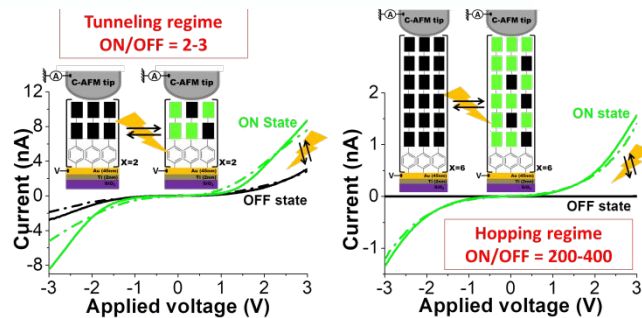
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TOC graphic: