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Unprecedented ON/OFF ratios in photoactive diarylethene-bisthienylbenzene molecular junctions

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ABSTRACT. Photoactive molecular junctions, based on 4 nm-thick diarylethene (DAE) and 5 nm-thick bisthienylbenzene (BTB) layers, were fabricated by electrochemical deposition. Total thickness was around 9 nm, *i.e.* above the direct tunneling limit and in the hopping regime. The DAE units were switched between their open and closed forms. The DAE/BTB bilayer structure exhibits new electronic functions combining photoswitching and photorectification. The open form of DAE/BTB shows low conductance and asymmetric IV curves while the closed form shows symmetric IV curves and high conductance. More importantly, unprecedented ON/OFF current ratios of over 10 000 at 1 volts were reproducibly measured.

KEYWORDS. photoswitch; electroswitch; diarylethenes; modified surfaces; molecular junctions,

MAIN TEXT. Photochromic molecules, *i.e.* molecules with two different forms (open/non-conjugated and closed/conjugated) which can be interconverted by light irradiation, have been proposed as building blocks for photoresistive switches in molecular electronics.^{1,2} Most studies devoted to the transport characteristics in such systems, have been limited to monolayer-based or single-molecule-based molecular junctions (MJs) where the dominant transport mechanism is direct tunneling.³⁻⁶ In this regime, photoswitching shows poor reversibility^{7,8} and small ON/OFF ratios (less than two orders of magnitude) due to strong molecule-electrode coupling which induces quenching effects,⁹⁻¹¹ and it is only recently that a high ON/OFF ratio (around 100) with good reversibility was reported, using a strategy that decouples the active unit from the electrode.¹²

When the thickness of the layer incorporated in an MJ is above 5 nm the main transport mechanism is hopping, which has a stronger molecular signature than tunneling.^{13,14} MJs incorporating photochrome-based layers above 5 nm thick have been studied¹⁵⁻¹⁸ while two recent studies^{19,20} have compared the performances of photoactive devices in both regimes. In the first,¹⁹ junctions showed ON/OFF ratios of 10 and were not significantly affected by the length of the wire. In contrast, we recently demonstrated that ON/OFF ratios increase from 2-3 to 200-400 for 3 nm and 9 nm-thick diarylethene-based layers, respectively. This improvement was explained by the OFF state of the thicker devices being much less conductive than that of the thinner ones, while the conductance of the ON states is similar.

We have now prepared 9 nm-thick MJs using a bilayer system. The first layer (5 nm) is based on bithienylbenzene oligomers, (BTB), which are known to be good molecular wires and show activation-less transport and low attenuation factors in the hopping regime.²¹ The second layer (around 4 nm) is based on photochromic diarylethene oligomers, (DAE).

The layers were grafted one over the other on gold by diazonium salt electroreduction. Our aim is to compare the photoresponse of the bilayer system with that of a 9 nm-thick DAE single layer, *i.e.* in the same transport regime, in MJJs using a C-AFM tip as the top electrode (Figure 1). It is found that the conductance of both MJJs can be reversibly switched, and that the ON/OFF ratios increases from 200-400 for DAE-based MJJs to an unprecedented value of 10 000 for the DAE/BTB bilayer system, thanks to the much higher conductance of the ON state.

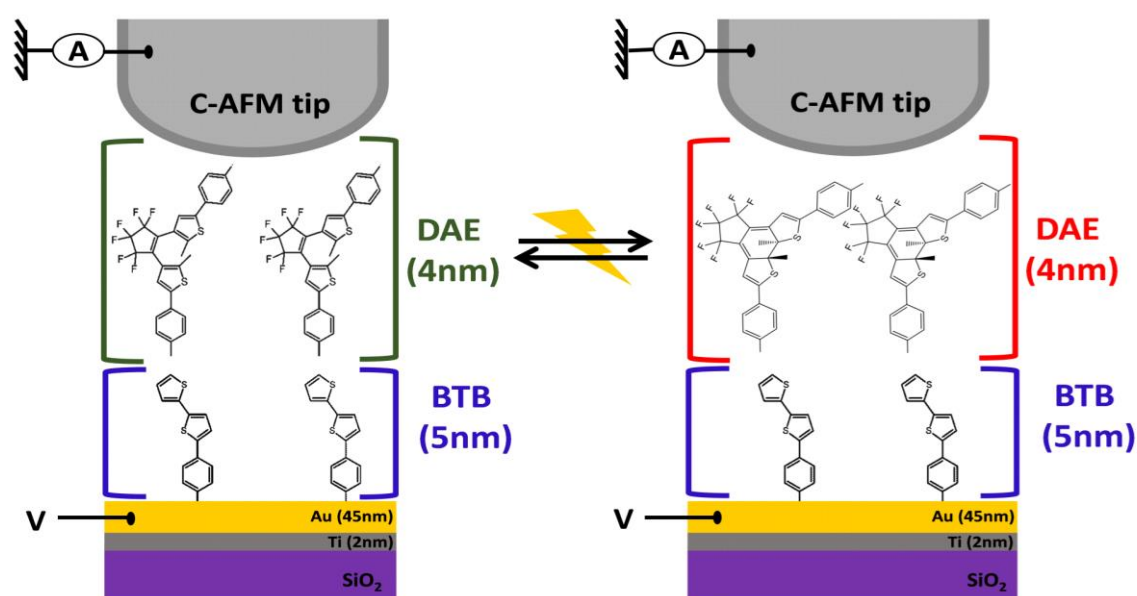


Figure 1. Schematic illustration of SiO₂/Ti₂/Au/BTB/DAE/C-AFM tip (Pt/Ir) molecular junction and the photoswitch of the oligo(DAE) units. The switch is turned ON by UV and OFF by visible light.

1-(2-Bisthienyl)-4-aminobenzene (BTAB) and perfluoro-1,2-bis(2-(4-aminophenyl)-5-methylthien-4-yl)cyclopentene (DAE-(C₆H₄NH₂)₂) were synthesized by known procedures.^{8,22} They both incorporate aniline groups for grafting and thiophene units (Figure S1a and S1b). The photoswitching and electrochemical properties of DAE-(C₆H₄NH₂)₂ in solution are described in the Supporting Information. Briefly, the open form shows one

irreversible peak for aniline oxidation at 0.81 V/SCE. The closed form shows another reversible redox signal for DAE core oxidation at 0.47 V/SCE (Figure S1c). These results indicate that the HOMO of the closed form of DAE is almost in resonance with that of BTB, while that of the open form is way below.

The aniline groups were used for *in situ* diazonium generation and layer deposition on a gold surface. BTB was first grafted onto a bare 45 nm-thick Au electrode deposited on a Si/SiO₂ wafer (Figure S2a). Next, DAE was grafted onto the BTB/Au electrode using a similar procedure (Figure S2c) (See the Supporting Information for more details). Figure S3 show the thickness measured by AFM after each deposition step: BTB 4.9 nm and DAE 4.1 nm. The roughness of the DAE/BTB layers measured by AFM is around 1 nm (Figure S4), close to that for bare Au (0.8 nm): the total thickness is 9±1 nm. The DAE/BTB layers were characterized by X-ray photoelectron spectroscopy (XPS), (Figure S6) which further confirms the over-grafting of the DAE units on the first layer of BTB to form a bilayer on the Au electrode (more details are provided in the Supporting Information).

The layers were also characterized by cyclic voltammetry. Figure 2A and 2B show the response of decamethylferrocene (DmFc) and ferrocene (Fc) on a bare electrode, a BTB/Au electrode and a DAE/BTB/Au electrode with DAE in its open form (noted DAEo in the following).

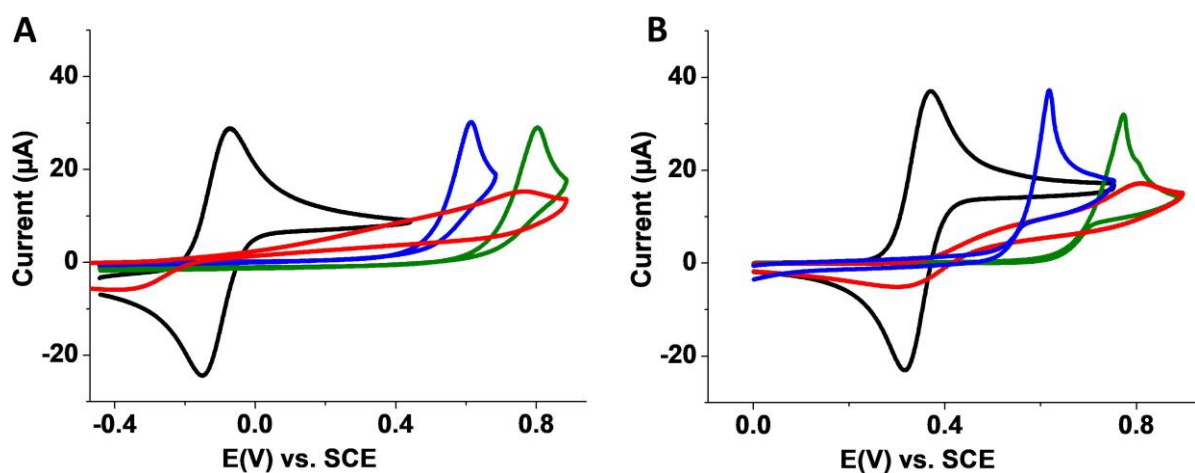


Figure 2. Characterization of DAE/BTB-modified gold surfaces by electrochemistry: (A) Decamethylferrocene and (B) ferrocene responses (5 mM solutions in acetonitrile) on bare (black), BTB-modified (blue) and DAE-modified electrodes before (green) and after (red) UV light irradiation. Supporting electrolyte 0.1 M TBAPF₆, scan rate 0.1 V.s⁻¹.

The usual reversible signal of the redox probes on the bare electrode (Figure 2, black curves) becomes an irreversible signal on the BTB/Au electrode (Figure 2, blue curves). This phenomenon has already been described many times and indicates that BTB layers can reversibly switch from an insulating to a conductive state at a potential close to 0.5 V/SCE.^[10] As a consequence, the DmFc and Fc oxidation peaks on this electrode are shifted to 0.5-0.6 V as they can only be oxidized at a potential above the switching potential of the BTB layer (Note also that both probes are oxidized at the same potential (Figure S8a) despite the fact that their standard redox potentials are different). Another consequence is that DmFc⁺ and Fc⁺ cannot be reduced in the reverse scan, since the BTB film is back in its insulating form at -0.2 V and 0.3 V where DmFc⁺ and Fc⁺, respectively, usually start to be reduced on a bare electrode. When DmFc and Fc are oxidized on a DAEo/BTB/Au electrode, the signals are again irreversible but the oxidation peaks of both probes are further shifted to 0.8 V/SCE (Figure S2, green curves). Here again both probes are oxidized at the same potential (Figure S8b) and there are no reduction signals on the reverse scans. This clearly shows that DAEo has been grafted onto the BTB/Au electrode. The new layer still exhibits switching behavior, thanks to the oligothiophene backbone of the film, but at a higher potential than that of the initial BTB layer. This suggests that the BTB and DAEo units are covalently bonded to each other. Next these DAEo/BTB/Au electrodes were irradiated with UV light to look for photoactivity induced by the DAE units. The red curves in Figure 2A and 2B show DmFc and Fc signals on UV-irradiated DAE/BTB electrodes. DmFc and Fc can now be oxidized and

reduced at potentials close to those for a bare electrode. This indicates that some DAEc units (DAE in its closed form) have been generated on the surface by irradiation and act as electron relays and/or generate nanopores in the initial layer. The number of DAE units undergoing this switch remains unknown but is high enough for the layer to become partially transparent towards the probes. An exciting and unique result, demonstrated by electrochemistry, is that DAE/BTB/Au electrodes show double switching, one associated with the oligothiophene-based backbone, triggered by the applied potential and changing the conductivity of the layer (p-doping), and a second one, triggered by light, based on the interconversion of the photochromic DAE units, alternating between open/non-conjugated and closed/conjugated forms.

Next, we grafted these molecules onto gold microelectrode stripes (20 μm x 2 cm and 45 nm-thick on Ti/SiO₂). The total thickness is around 9 nm (DAE ~4nm; BTB ~5nm) and can therefore be easily compared with previous results obtained from DAE or BTB single layers with similar thicknesses and measured under similar conditions with identical contacts. To investigate the electronic properties of the bilayer deposited on gold, a C-AFM tip was used as the top electrode to complete the junction. The current versus voltage *IV* data from these experiments are summarized in Figure 3. More data can be found in Figure S10. Each curve represents an average of 200 *IV* traces in several positions using the same applied force (~2.5 nN) (more details are provided in the Experimental section). The measurements were performed four times, starting with the initial state where the DAE units have been grafted in their stable open form. This form is associated with the OFF state (green curves, Figure 3). Then, the junctions were irradiated by UV light (at 365 nm) for 1 hour in order to reach a photostationary state with a high closed-form content. This form will be labeled the ON state in the following, as the conjugation extends over most of the photochrome (red curves, Figure 3).

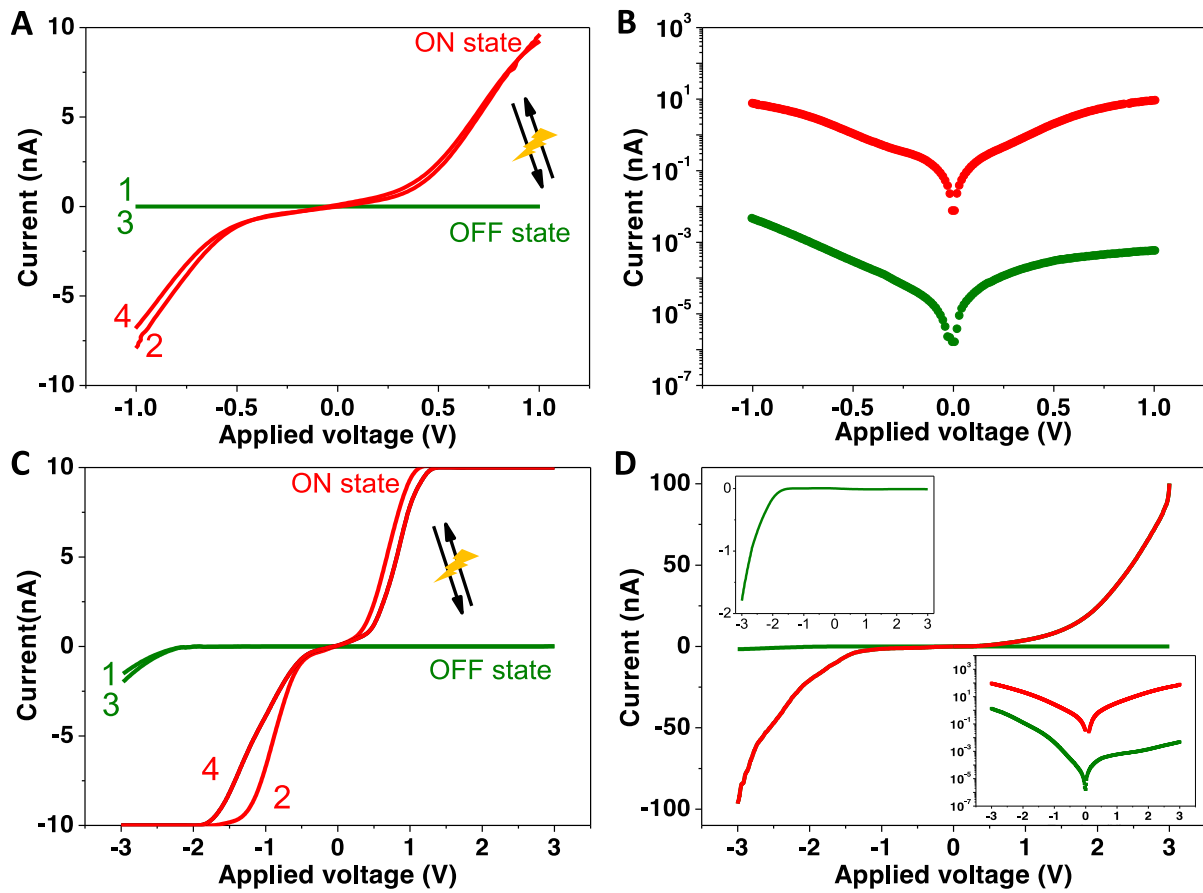


Figure 3. Transport characteristics of the DAE/BTB bilayer junctions measured by C-AFM before (green curves) and after (red curves) UV irradiation at room temperature. (A) IV curves between -1 and 1 V. (B) Same data in $\log(I)$ versus V format for direct visualization of the ON/OFF ratio. (C) IV curves between -3 and +3 V using C-AFM set-up, showing reversibility and rectification in the OFF state. (D) IV curves between -3 and +3 V using a resiscope set-up; upper left inset, zoom on the OFF state IV curve; lower right inset, same data in $\log(I)$ versus V format.

A strong switch of the transport properties of the bilayer MJJs is observed (Figure 3A) upon light irradiation and can be attributed to a change of the isomerization state of the DAE layer. The junction is highly resistive when the DAE units are in their open photostationary

state. The current does not exceed a few picoamps at 1 V while it reaches 9 nA at 1 V in the ON state after irradiation with UV light (closed form). Figure 3B shows the same data in $\log(I)$ versus V format. It allows direct visualization of the ON/OFF ratio, which reaches an unprecedented value of 10 000 at 1 V. Figure 3C expands the voltage range to +3 V and shows that the IV curve in the OFF state (Figure 3, curve #1) is not symmetrical anymore. This device rectifies the current, the preferred current direction being obtained when a negative voltage is applied to the bottom electrode. Switching to the ON state shows a saturated IV curve (Figure 3, curve #2) above 1.2 V, indicating that the junction conductance is so high that the C-AFM amplifier can no longer measure the current. Figure 3C also shows that switching between ON and OFF states is reversible (Figure 3C, curves #3 and #4) upon irradiation by visible light (0.5 hour at 435 nm) followed by UV light. Finally, Figure 3D shows the IV curves recorded using an AFM equipped with a resiscope module. This system allows IV measurements with current varying over seven orders of magnitude and, consequently, that between -3 and +3 V can be measured in both states. In the ON state this current reaches 90 nA at -3 and +3 V and the IV curve is symmetrical with no preferred direction, whereas in the OFF state it is only few picoamps at +3 V, and -1.8 nA at -3 V. Rectification in the OFF state is best seen in the left inset of Figure 3D; the rectification ratio reaches 200 at +3 V. The ON/OFF ratio of the MJ remains at 10 000 at 3 V while it decreases to 50 at -3 V, as displayed in the right inset of Figure 3D.

Previous studies have been performed under the same experimental conditions (with the same bottom and top electrodes) but using DAE in a 3 or 9 nm-thick single-layer MJ. Figure 4 compares the results in $\log(I)$ versus V format. In $DAE_{3\text{nm}}$ MJs (Figure 4A), the dominant transport mechanism is direct tunneling while in those using $DAE_{9\text{nm}}$ (Figure 4B) and in the systems reported here (Figure 4C) hopping prevails. In this regime, a strong

molecular signature on the electronic response of the junction is revealed and much higher ON/OFF ratios are observed.

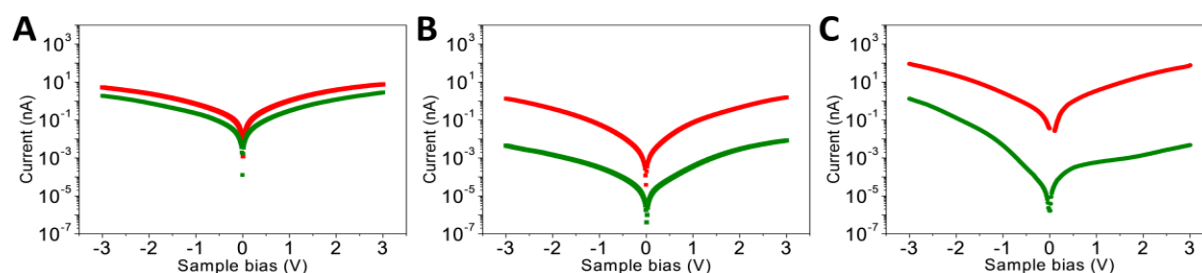


Figure 4. $\log(I)$ versus V characteristics before (green) and after (red) UV irradiation of: (A) DAE_{3nm}, (B) DAE_{9nm} and (D) DAE_{4nm}/BTB_{5nm} junctions measured by C-AFM up to +3 V.

Adding a first layer of BTB as an electroswitchable molecular spacer, between the DAE units and the bottom electrode, while keeping the same overall junction thickness (~9 nm), causes considerable changes in the transport properties of the devices. New electronic functions combining photorectification and photoswitching are observed. Indeed, a first important result is that the IV curves of the bilayer before irradiation are asymmetric, with preferred current flow for negative polarization and rectification around 200 at +3 V. Rectification disappears upon switching to the ON state. More importantly, giant ON/OFF ratios above 10 000 between -1 and +1 V and at +3 V are obtained. These easily reproducible results (Figure 3C and S11) present the highest ON/OFF conductance ratios obtained in solid-state photoswitches based on photochromic molecules. This improvement is due to the fact that the ON state of the bilayer devices is much more conductive than that of the DAE_{9nm} single-layer devices while the conductances of the OFF states are similar. This extremely high conductance of the ON state of the DAE/BTB MJs may come from the HOMO levels of the closed form of DAE and BTB, which are almost in resonance, and to the electroswitchable properties of BTB (p-doping) which can reduce the effective transport distance. The ON/OFF

ratio may also be enhanced by the BTB spacer which probably limits the quenching effects^{7,8,23} of the bottom electrode on the yield of the DAE photoswitch interconversion.

This work shows that molecules with electro- and photoswitchable properties can be combined in solid-state devices to develop new and key components for future nanoelectronics. Electrochemical engineering designed to control coupling between molecules has been the key to our success in constructing photorectifiers and photoelectrical switches.

Methods Section.

Layer electrografting: Equipment for electrochemical experiments were described in a previous publication.^[5] An acetonitrile (ACN) solution containing 0.5 mM of BTAB or 0.5 mM of DAE-(C₆H₄NH₂)₂ in its open form and 0.1 M of tetrabutylammonium hexafluorophosphate (TBAPF₆⁻), as a supporting electrolyte, was used. The diazonium cations were generated *in situ* from the corresponding amine by adding 10 equivalents of tBuONO. Before grafting, the solutions were deoxygenated by bubbling argon for at least 15 min. Then, cyclic voltammetry was used to deposit the molecular layers. After each grafting, the modified electrodes were copiously rinsed in an ACN solution to remove all physisorbed molecules from the deposited layers.

Layer Characterization: AFM measurements were performed using a Nano-Observer AFM microscope (CS Instruments AFM Microscopes, France). Images were recorded in the tapping mode with a tip from Budgetsensor (AFM tap 300 G, resonance frequency 300 kHz, force constant 40 nN/m) and the height histogram plotted by SPIP software.

The XPS spectra were determined with a Thermo VG Scientific ESCALAB 250 system with Al K α ray (1486.6 eV, 500 μ m beam) excitation. The measurements were performed at below 5.10⁻⁷ mbar and were calibrated with respect to the 1s carbon peak which was set at 285.

C-AFM Junction formation and measurement: Molecular junctions were formed by bringing a conductive tip into contact with a layer. These measurements were performed using a Nano-Observer AFM microscope (CS Instruments AFM Microscopes, France). The AFM head was kept under an inert atmosphere (argon) during the measurements. A Cr/Pt conductive coated tip from Budgetsensor (ContE-G, resonance frequency 13 kHz, force constant 0.2 nN.m^{-1}) was used as top electrode to complete the MJs and all the *IV* curves were recorded in the contact C-AFM mode (in this mode, the sensitivity of the current is limited to $\pm 10 \text{ nA}$). To make a reproducible soft contact, an applied force of 2.5 nN^{24} was used in all the measurements and checked after every change of the position on the sample. A calibration study was first performed to test the C-AFM tips on alkanethiol monolayers (an effective calibration standard). An example is given in Figure S9. It shows conductivity similar to that given in the literature for the alkanethiol monolayers of various length (with a number of carbon $n = 6, 8$ and 10).²⁵ Then the measurements were done on our Au stripes modified by the bilayer junctions. Furthermore, in order to study the reproducibility and to have access to a larger current range, the measurements were repeated using the same Nano-Observer AFM microscope equipped with a resiscope module, the other experimental conditions being the same. This system allows *IV* measurements with current varying over seven orders of magnitude. After electrical measurements, all samples were stored in vacuum.

Samples were photo-irradiated with a xenon lamp using filters between the lamp and the samples. These filters were centered at 365 nm for UV light and 435 for visible light. In order to switch a maximum of molecules to the ON or the OFF state on the surface, the samples were analyzed immediately after being exposed to UV or Vis light for 1 hour or 0.5 h, respectively.

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ASSOCIATED CONTENT

Supporting Information Available: UV–vis spectra, electrochemical deposition, AFM, XPS analysis, and *IV* curve. This material is available free of charge *via* the Internet at

<http://pubs.acs.org>.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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