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**COMMUNICATION** Philippe Blanchard, Jean Roncali *et al.* Oligothiophene-derivatized azobenzene as immobilized photoswitchable conjugated systems

## Oligothiophene-derivatized azobenzene as immobilized photoswitchable conjugated systems<sup>†</sup>

Sandrine Karpe,<sup>a</sup> Maïténa Oçafrain,<sup>a</sup> Kacem Smaali,<sup>b</sup> Stéphane Lenfant,<sup>b</sup> Dominique Vuillaume,<sup>b</sup> Philippe Blanchard<sup>\*a</sup> and Jean Roncali<sup>\*a</sup>

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Immobilization of an azobenzene-bithiophene compound on a gold surface leads to self-assembled monolayers with photoswitchable electrical properties.

Surface-immobilization of light-stimulable  $\pi$ -conjugated molecules as self-assembled monolayers (SAMs) is the focus of high current interest.<sup>1</sup> Azobenzene is known to reversibly switch between an extended *trans* to a shorter *cis* configuration upon irradiation at *ca*. 360 nm and 480 nm, respectively. Azobenzene derivatives have been grafted on surfaces in view of various applications in molecular electronics,<sup>2</sup> molecular machines,<sup>3</sup> photoswitchable wettability,<sup>4</sup> photoinduced magnetization<sup>5</sup> and modulation of interactions of surfaces with biomolecules<sup>6</sup> or metal cations.<sup>7</sup>

Azobenzene-based molecular or nano-junctions that exhibit conductance switching with *trans/cis* photoisomerization have been recently reported.<sup>2*a,c,d,*3,8</sup> In this context, the development of molecular architectures that could lead to high on/off current ratio between the two configurational states appears as a valuable goal.

Efficient reversible *trans/cis* isomerization of immobilized azobenzene derivatives requires a decoupling of the azobenzene unit from the surface in order to prevent or limit the quenching of the photo-excited state by the metal substrate.<sup>8</sup> To this end, azobenzene units have been covalently fixed on metal surfaces through different spacers such as alkane chains,<sup>2a,5,6b,9</sup> aryl units,<sup>2d,2f,10</sup> or interfacial platforms.<sup>4a,11</sup>

In this work part of the long electrically insulating alkyl spacers generally used to improve the formation of SAM from thiol-terminated molecular systems has been replaced by an electron-rich bithienyl  $\pi$ -conjugated system. Besides possible  $\pi$ - $\pi$  intermolecular interactions in the SAM, the incorporation of a conjugated segment redox active at moderately positive potentials will allow for preliminary characterization of the immobilization process by means of simple electrochemical experiments.<sup>12</sup>

In the continuation of our work on photo-stimulable  $\pi$ -conjugated systems,<sup>13</sup> we present here the synthesis and characterization of the electronic properties of thioester 1, the preparation of electroactive monolayers of 1-SH on a gold surface and preliminary results on their photoswitchable electrical properties.

The synthesis of compound 1 is described in Scheme 1. Compound 2 was prepared from 2,2'-bithiophene by a double lithiation followed by successive additions of elemental sulfur and 3-bromopropionitrile according to known procedures.<sup>14</sup> Reaction of 2 with one equivalent of caesium hydroxide led to the selective deprotection of one thiolate group which was reacted with a slight excess of bromomethyl azobenzene 3 to give compound 4 in 60–67% yields. Compound 3 was prepared in 62% yield from 4,4'-dimethylazobenzene (*p*-diMeAB) by reaction with 2 equiv. of NBS in the presence of a catalytic amount of ZrCl<sub>4</sub> as Lewis acid (see SI<sup>†</sup>).

Treatment of compound 4 with one equiv. of caesium hydroxide and subsequent addition of a slight excess of thiol ester  $5^{15}$  gave the target compound 1 in 74–78% yield.



Scheme 1 Synthetic route to 1 and 1-SH.

<sup>&</sup>lt;sup>a</sup> University of Angers, CNRS, CIMA, Linear Conjugated Systems Group, 2 Bd Lavoisier, Angers 49045, France. E-mail: philippe.blanchard@univ-angers.fr, jean.roncali@univ-angers.fr;

*E-mail:* philippe.blanchara@univ-angers.jr, jean-roncau@univ-angers.jr,  $Fax: +33 \ 241 \ 73 \ 54 \ 05; \ Tel: +33 \ 241 \ 73 \ 50 \ 59$ 

<sup>&</sup>lt;sup>b</sup> Molecular Nanostructures & Devices Group, Institute for Electronics, Microelectronics and Nanotechnology, CNRS & University of Lille, B.P. 60069, 59652, Villeneuve d'Ascq, France

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Saponification of **1** by caesium hydroxide followed by addition of HCl gave monothiol **1-SH** in 80% yield.

The UV-vis absorption spectrum of bithiophene **2** shows a  $\pi-\pi^*$  absorption band at 339 nm whereas that of *p*-diMeAB exhibits two absorption bands characteristic of the azobenzene unit, an intense band ( $\lambda_{max} = 336$  nm) corresponding to the  $\pi-\pi^*$  transition and a broad weak band ( $\lambda_{max} = 440$  nm) related to the n- $\pi^*$  transition. As expected, the spectrum of **1**, **1-SH** and **4** shows an intense band at 339–342 nm and a weak band at 435–440 nm. The band around 340 nm corresponds to the convolution of the  $\pi-\pi^*$  transitions of the 5,5'-disulfanyl-2,2'-bithiophene segment and the azobenzene moiety, in agreement with the higher molar extinction coefficients of **1**, **1-SH** and **4** relative to those of **2** and *p*-diMeAB (Table S1<sup>†</sup>).

As shown in Fig. 1, irradiation of a solution of compound 1 at 360 nm produces a progressive decrease of the intensity and a slight broadening of the 342 nm band with an increase of the absorbance of the n- $\pi^*$  transition in the 400–450 nm region. The presence of two isosbestic points at 297 nm and 380 nm indicates the coexistence of two chemical species in equilibrium. These results are in full agreement with the *trans/cis* isomerization of the azobenzene moiety of 1. Irradiation with 480 nm monochromatic light induces the reverse *cis/trans* isomerization although a photostationary state is reached before complete return to the initial conditions (Fig. S2†).

The cyclic voltammogram (CV) of compounds 1, 2 and 4 exhibits two reversible one-electron oxidation waves corresponding to the successive formation of the radical cation and dication of the dialkylsulfanyl-bithiophene system at anodic peak potentials of  $E_{pa}^{1} = 1.00-1.16$  V and  $E_{pa}^{2} = 1.17-1.29$  V respectively (Fig. S3†). The stability of the oxidized states can be explained by the strong + *M* electron-donating effect of the two sulfide groups.<sup>16</sup> In the case of **1-SH**, the first oxidation wave associated with the formation of the radical cation was slightly broadened due to the concomitant irreversible oxidation of the thiol group into disulfide (Fig. S3†).

Monolayers of **1-SH** have been prepared by immersion of gold electrodes in  $CH_2Cl_2$  solutions of freshly generated **1-SH** in the absence of light. Fig. 2 shows the typical CV trace of a monolayer of **1-SH**. The CV exhibits a reversible one-electron



**Fig. 1** Changes in the UV-vis spectrum of **1** in  $CH_2Cl_2$  ( $4 \times 10^{-6}$  M) at 20 °C after photoirradiation at 360 nm for 0, 20, 45, 105, 165, 225, 285 and 345 min.



Fig. 2 CV of a monolayer of 1-SH on gold immersed in 0.1 M n-Bu<sub>4</sub>NPF<sub>6</sub>/CH<sub>3</sub>CN-CH<sub>2</sub>Cl<sub>2</sub> 1:1, scan rate 1000 mV s<sup>-1</sup>. Insert: variation of the intensity of the oxidation peak *vs.* scan rate.

oxidation wave at  $E_{pa}{}^{1} = 0.98$  V associated with a cathodic peak at 0.95 V. The analysis of the CV response of the monolayer at different scan rates ranging from 50 to 8000 mV s<sup>-1</sup> reveals a linear variation of the peak current vs. scan rate with an invariance of  $E_{pa}{}^{1}$  (Fig. 2, insert). These results are consistent with a fast redox reaction of a surfaceimmobilized species. The determination of the surface coverage by integration of the CV wave gave (after correction for double-layer charge) a value of  $4 \times 10^{-10}$  mol cm<sup>-2</sup> consistent with a densely close-packed monolayer.

Photo-switching of the SAM was tested by focusing monochromatic light through an optical fiber. Preliminary results show that the water contact angle reversibly switches from  $93 \pm 2^{\circ}$  after irradiation at 360 nm (*cis* isomer) to  $98 \pm 2^{\circ}$  after irradiation at 480 nm (*trans* isomer). In parallel, the thickness of the SAM measured by ellipsometry switches from  $25 \pm 1$  Å (*cis* isomer) to  $30 \pm 1$  Å (*trans* isomer). These results are in full agreement with the *trans/cis* photo-isomerization of the immobilized **1-SH** molecules.

The photoinduced changes of the electrical properties of the SAMs were analyzed by recording current vs. voltage (I/V)curves of the junction formed between the gold substrate and the metallic tip of a conducting-AFM. Fig. 3 shows the typical I-V curves for a pristine SAM, after 90 min exposure to 480 nm light (trans isomer), and after 90 min irradiation at 360 nm (cis isomer). From these two latter curves, where the higher conductance state is associated with the cis isomer, a typical on/off ratio is determined with a maximum of  $3-4 \times 10^3$  at  $\pm 1.6$  V, irrespective of the sign of the applied bias. Mayor and coworkers<sup>2d</sup> have recently reported an on/off ratio of about 25-30 for SAMs based on a biphenyl-based azobenzene derivative and attributed the observed changes in conductance to the variation of the layer thickness. However, the much larger on/off ratio observed here suggests that in addition to purely geometrical effects, photo-induced changes in the electronic structure of the junction can also play a role. In fact, a detailed analysis of the I-V curves of the trans and the cis isomers shows that the difference between the electrode Fermi energy and the LUMO energy is lowered by ca. 0.4 eV



Fig. 3 Current vs. voltage (I-V) curves measured by C-AFM (load force 20–30 nN, V applied on the Au substrate of the sample) on a pristine SAM immediately after its formation, after irradiation at 360 nm for 90 min (*cis* isomer) and after irradiation at 480 nm for 90 min (*trans* isomer).

for the *cis*-isomer, in good agreement with first principles DFT calculations (0.53 eV).<sup>17</sup>

In summary, compound 1 has been readily synthesized by connecting an azobenzene and a 2,2'-bithiophene unit thanks to thiolate chemistry. The corresponding thiol compound forms stable electroactive monolayers on a gold surface with fast surface-confined electrochemical response. Preliminary results show that after surface immobilization, the molecules undergo reversible *trans/cis* photoisomerization with a concomitant conductance switch with very high on/off current ratio. The relationships between the molecular structure, the properties of the molecular junction and the photo-induced changes in electrical properties are now subject to detailed experimental and theoretical investigations and will be reported in a forthcoming publication.<sup>17</sup>

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