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Tunable Electrochemical Switches Based on Ultrathin Organic Films

Claire Fave, Yann Leroux, Gaelle Trippé, Hyacinte Randriamahazaka, Vincent Noel,* and Jean-Christophe Lacroix*

Interfaces, Traitements, Organisation et Dynamique des Systèmes, Université Paris 7-Denis Diderot, UMR 7086, 1 rue Guy de la Brosse, 75005 Paris, France

Received November 20, 2006; E-mail: noel@itodys.jussieu.fr; lacroix@paris7.jussieu.fr

During the last two decades, there has been considerable interest in replacing conventional inorganic semiconductors with organic materials in optical and electronic devices. Among organic materials, since the seminal work of Aviram,[1] conjugated polymers (CPs) have been proposed and used as basic building blocks in molecular electronics. Thus intense research efforts are being devoted to understanding electron transport and electron transfer on the nanoscale within such molecules or through metal/oligomer/metal junctions.[2,3] One of the most important properties of CPs is their ability to switch upon chemical or electrochemical doping between two states with different electronic characteristics. Their electrochemical switching has been demonstrated to be an easy means of controlling the properties of grafted molecules[4] and of metallic nanoparticles.[5] To realize efficient organic electronic devices based on a few electron transfers, progress in triggering the properties of grafted groups must be made in order to control the interface between CP units and metallic electrodes. A monolayer junction based on conjugated oligomers, with a well-defined metal/oligomer interface retaining reversible *on/off switching* capabilities controlled by the redox state of the oligomer would be of interest for molecular electronics.

We report here the properties of ultrathin organic films on glassy carbon (GC) or polycrystalline gold obtained by electroreduction of diazonium salts. This method allows the preparation of very thin organic layers with covalent bonding to the electrode[6,7] (see Figure 1a).

The organic film was obtained by cycling a GC or gold electrode in a solution containing the diazonium salt of 1-(2-bisthienyl)-4-aminobenzene (BTAB). Grafted molecules will be noted BTB. Supporting Information describes this electrochemical process. On the basis of the area of the reduction peak during the modification of the GC electrode surface with the diazonium salt, the coverage of the BTB moieties was calculated to be around 2×10^{-9} mol·cm^{-2} (note that this procedure does not yield to a precise value since grafting efficiency will not be of 100%). The reported surface coverage on GC substrates[8] varies in the range of 4 to 12×10^{-10} mol·cm^{-2} with the theoretical maximum surface coverage for a monolayer on GC surfaces being around 10^{-9} mol·cm^{-2}. The surface coverage of 2×10^{-9} mol·cm^{-2} clearly indicates that the GC electrode is modified with a few monomolecular layers rather than with a thick film of BTB molecules. Similar results are obtained on gold. Surface probe microscopy has been used to probe the organic layer thickness (see Figure 1b). Since the GC substrates show high surface roughness, we performed AFM scratching experiments (see Supporting Information) on gold substrates and obtained an average depth of 5.8(±0.4) nm for the BTB film thickness. If the size of the grafted BTB is estimated to be 12.6 Å, the layer is not monomolecular, in agreement with previous reports.[9,10]

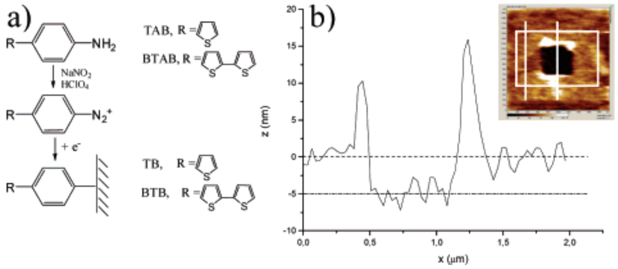

Figure 1. (a) Formation of organic film by electroreduction. (b) Lines profile through a scratch of a BTB film. Inset: 2 × 2 μm image showing a 500 × 500 nm scratch formed with contact mode AFM.

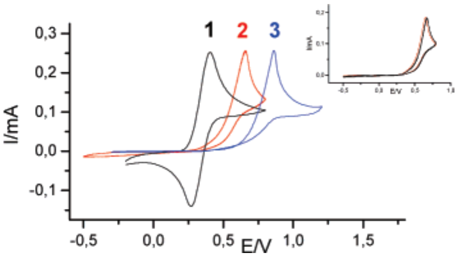

Figure 2. Cyclic voltammetry in ACN + 0.01 M Fc + 0.1 M LiClO$_4$ solution of (**1**) bare GC, (**2**) BTB, and (**3**) TB electrodes. Inset: (red) first scan and (black) five successive scans, scan rate 0.1 V/s.

Electroactivity of the film was then studied in a solution of LiClO$_4$ in acetonitrile (see Supporting Information). A wave with a threshold around 0.5 V/SCE is observed in the cyclic voltammetry of a BTB-modified GC electrode. Multiple cycles show no degradation of this signal when the inversion potential is kept below 1 V.

Fresh BTB-modified GC electrodes were then plunged into a ferrocene (Fc) solution to probe their electrochemical behavior toward reversible outer-sphere redox species. Figure 2 compares the Fc electrochemical response on bare and BTB-modified GC electrodes. No current is observed on the BTB-modified electrode in the potential range where Fc redox reactions usually occur on bare electrodes. The organic layer totally blocks the electrode in such a potential window. Above 0.5 V/SCE, the current dramatically increases and an "irreversible" wave is observed with an oxidation peak at 0.65 V as compared to 0.4 V on the bare electrode. Such an electrochemical signal suggests at first sight an EC mechanism, but a ring-disk experiment, where the disk is a BTB-modified GC electrode, shows that the species generated in this wave is ferrocenium and can be collected on the ring (at a potential characteristic of the Fc$^+$/Fc redox couple). The "irreversible" wave shows a diffusion-controlled profile with I_p scaling linearly with $v^{1/2}$ and the Fc concentration within the investigated sweep rate (and concentration) as expected for the oxidation peak of a simple reversible system. The peak shape is also identical on both the bare and modified GC electrodes, suggesting that the heterogeneous rate constant for Fc oxidation is similar on both substrates. This behavior is in marked contrast with results already published by several

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groups where strong peak shape deformation is associated with a significant decrease in the heterogeneous rate constant. However, in these previous studies, both anodic and cathodic Fc peaks were seen, which makes it possible to evaluate the heterogeneous rate constant decrease by measuring ΔE_P. In the present case, no peak for Fc^+ reduction is observed even at very cathodic polarization during the reverse potential scan. Another feature is the stability of the electrochemical response in successive scans (cf. Figure 2, inset).

To the best of our knowledge, no examples exist in the literature describing such ultrathin organic layers displaying this electrochemical behavior. McCreery et al.[11] have studied biphenyl molecular layers. Initially, the film is described in an "off", low conductivity state, and Fc electroactivity is slower than on bare GC. However, after cathodic polarization of the modified electrode, they observe that the Fc electrochemical response is modified and is now similar to that on bare GC. They interpret these results in terms of organic layer conductance switch, and in their scheme, an "on" of high conductivity state is reached under cathodic polarization. However, no reversibility of the on/off switch was observed.

Charge transfer from one electrode to a redox group separated by an organic linker assembled in the form of a dense monolayer has been extensively studied.[12] For an ideal monolayer with no pinholes or defects, electron transfer occurs through the layer. Electron tunneling is usually used to describe the barrier properties of such organic layers. The tunneling current is a function of the intrinsic properties of the bridge (HOMO/LUMO gap) and the electron tunneling distance. For film thicknesses above a few nanometers, coherent tunneling is not efficient. The value of 5 nm found for BTB layers is too high for tunneling through molecules with a large HOMO−LUMO gap to be the main electron transfer mechanism.

In the case of electron transfer through pinholes or defects, the peak current would be smaller than that on a bare electrode, especially in the case of nonspherical diffusion.[7,13,14] Thus, electron transfer is likely to occur through the BTB layer by a sequential mechanism for a potential above a certain threshold. This threshold must be related to BTB oxidation potential as suggested by the apparent correspondence between BTB electroactivity in Fc free solution and the potential for Fc oxidation on BTB-modified GC. Following this idea, an $EC_{catalytic}$ mechanism consisting of two successive reactions could be first envisaged:

$$\mathrm{BTB} \rightarrow \mathrm{BTB}^{+\bullet} + e^- \tag{1}$$

$$\mathrm{BTB}^{+\bullet} + \mathrm{Fc} \rightarrow \mathrm{BTB} + \mathrm{Fc}^+ \tag{2}$$

In this case, the oxidation current will change with concentration and scan rate from a peak-shaped appearance to a sigmoid wave. This behavior is not observed experimentally here, and this scheme, therefore, has to be ruled out. An alternative sequential mechanism is a conductance reversible switch of the ultrathin organic film transport properties between off (blocking) and on (current flow) states, where BTB radical cations act as the molecular bridge. In the off state, BTB molecules are characterized by a large HOMO−LUMO gap, and with the film thickness of the film, no tunneling occurs through this organic barrier. Oxidation of BTB to BTB radical cations yields an organic layer with a much smaller HOMO−LUMO gap, and consequently, tunneling across this oxidized organic layer is much more efficient. (The question whether or not transport process within such low band gap tunneling barrier is coherent or incoherent is a separate question which will be addressed elsewhere.)[15]

A BTB electrode behaves as a reversible and reproducible electrochemical switch when the applied potential reaches a value close to the grafted BTB oxidation potential. Hence it ought to be possible to tune the threshold potential of the conductance switch by changing the number of thiophene units. In order to check this proposal, we have synthesized 1-(2-thienyl)-4-aminobenzene (TAB) and characterized the resulting organic electrodes. Gold and GC electrodes were modified via diazonium salt reduction and studied in the same manner as with BTB. AFM scratching measurements yield a layer thickness of 4.5(±0.7) nm. Figure 2 (curve 3) shows the electrochemical activity of Fc probes on the modified electrode. Once again, no current is observed near the normal potential of Fc, and a diffusion-controlled anodic peak is obtained at 0.86 V. As previously, the current increase is observed around the organic layer switching potential and above that for BTB layers. The anodic potential shift of the Fc oxidation peak (from BTB to TB layers) indicates that the switching potential depends, as expected, on the nature of the organic film.

We have shown that ultrathin organic layers constituting a reversible conductance switch can be obtained by electrografting diazonium salts onto a GC electrode. The organic electrodes switch reversibly between conducting and totally blocking states with a threshold voltage which can be tuned by carefully choosing the molecule grafted onto the electrode. Such junctions based on conjugated oligomers with a well-defined metal/oligomer interface retaining reversible on/off switching capabilities controlled by the redox state of the oligomer will be of interest as active interconnects for molecular electronics or in redox molecular actuators.

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Supporting Information Available: Electrochemical and AFM experimental details, BTB and TAB synthetic methods. This material is available free of charge via the Internet at http://pubs.acs.org.

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