

Grafting Oligothiophenes on Surfaces by Diazonium Electroreduction: A Step toward Ultrathin Junction with Well-Defined Metal/Oligomer Interface

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Abstract: The functionalization of electrode materials through diazonium electroreduction using a heteroaromatic compound, without phenyl groups, has been investigated for the first time. The electrochemical reduction of 2-aminoterthiophenyldiazonium cation, generated in situ, coats the electrode (glassy carbon (GC), gold or platinum) with an ultrathin organic layer, shown by X-ray photoelectron spectroscopy (XPS) of that deposited on gold to consist of terthiophene or oligothiophene. The coating is electroactive at potential close to that of terthiophene in solution. The electrochemical response of the modified GC electrode in the presence of various reversible redox couples shows that the attached layer acts as a conductive switch. It behaves as a barrier to electron transfer when the standard redox potential is below 0.5 V/SCE; in this case diode-like behavior is observed. However, for more oxidizing redox probes the layer can be considered as transparent and no barrier effect is observed. The layer deposited on a platinum ultramicroelectrode (UME) behaves similarly to that obtained on the large GC electrode. Scanning electrochemical microscopy (SECM) can be performed using this electroswitchable modified platinum UME which can act as a filter toward competitive redox exchange pathways.

Introduction

The attachment of organic molecules to carbon, metallic, and semiconductor-based substrates represents an interesting approach to the construction of novel interfaces and for bottom-up strategies in various fields. Among the numerous potential applications of such interfaces, some of the most interesting are the fabrication of molecular or plastic electronic devices,^{1,2} biosensing systems,³ anticorrosion coatings,⁴ and smart sur-

faces.⁵ Conjugated oligomers and, in particular, oligothiophenes (OTs) have been proposed and used as basic building blocks. One of the most important properties of OTs is their ability to switch, upon electrochemical or electrical doping, between two states with different electron transport properties. Electrochemical switching proves to be an easy means of controlling the properties of grafted molecules⁶ and of metallic nanoparticles⁷

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and is used in redox-gated single-molecule devices.⁸ Electrical doping of OTs in field effect transistors is the basis of their proposed use in molecular electronics and of their increasing use in low-cost plastic electronics. Nevertheless, to achieve efficient organic or molecular electronic devices based on a few electron transfers, progress must be made in controlling the interface between OT units and the metallic electrodes.

Oligothiophenes can be deposited using various techniques, either from solution (dip coating, self-assembly) or the vapor phase, or by electrochemical oxidation of a monomer. In such cases, the bond between the substrate and the deposited oligomers is not covalent and the interface is often ill defined. There are several reactions that lead to strong attachment of organic moieties to a surface. Many of these are induced by electron transfer to (or from) an organic molecule.^{9,10} The electroreduction of a phenyldiazonium salt (or a substituted phenyldiazonium salt)¹¹ produces phenyl radicals (and N₂), which bond covalently to the electrode.¹² This reaction has been investigated using various media^{13,14} and materials, such as metallic surfaces,^{15,16} carbon,¹⁴ and silicon.¹⁷ It yields ultrathin organic layers, since the deposit (grafted oligophenyl units) is insulating in the potential range required for further electrochemical reduction of the diazonium salt. The organic layer has been evidenced using several techniques: infrared spectroscopy, Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), atomic force microscopy, and cyclic voltammetry (CV), especially when an electroactive species is attached to the electrode (e.g., commonly the nitrophenyl group).^{12,18–20} However, the often observed growth of multilayer films illustrates the difficulty of controlling the amount of material deposited on the surface,^{20,21}

and prevents applications requiring the formation of a well-defined single monolayer. Establishing that there is a covalent bond between the aryl group layer and the electrode surface is a complex task which has been achieved only for carbon²² and iron surfaces.¹⁶ More recently theoretical calculations have shed some light on the type of these bonds for various substrates.²³ On the basis of these findings and the strong mechanical adherence of the layer, it is now widely accepted that covalent bonding between the organic layer and the electrode occurs.^{18,19} The first examples of diazonium-assisted modification of carbon electrodes were based on commercial or synthesized diazonium salts.²⁴ Later, in situ formation of the diazonium cation from aminophenyl compounds²⁵ by reaction with NaNO₂ in the presence of HClO₄ in an electrochemical cell was reported. This procedure involves simple reagents and requires no isolation and purification. By this route various substituted phenyldiazonium cations can be produced, and their electroreduction proceeds as with isolated diazoniums.²⁶ Moreover, this procedure makes it easy to select the molecules attached to the electrode surface with a view to the eventual application.

The present paper is devoted to the formation and the electrochemical investigation of a new diazonium cation, derived from a heteroaromatic compound, 2-aminoterthiophene. The in situ formation of the 2-terthiophenyldiazonium cation in the electrochemical cell, followed by its electroreduction at a glassy carbon (GC), gold, or platinum electrode, results in an ultrathin deposit of terthiophene or oligothiophene. Scheme 1 summarizes the synthesis, the generation of the diazonium cation, and its electroreduction. A modified gold electrode surface was analyzed by XPS. The electrochemical behavior of a modified GC electrode in the presence of different redox couples was characterized by CV. A modified platinum ultramicroelectrode (UME) was used to perform scanning electrochemical microscopy (SECM) approach curves.

Experimental Section

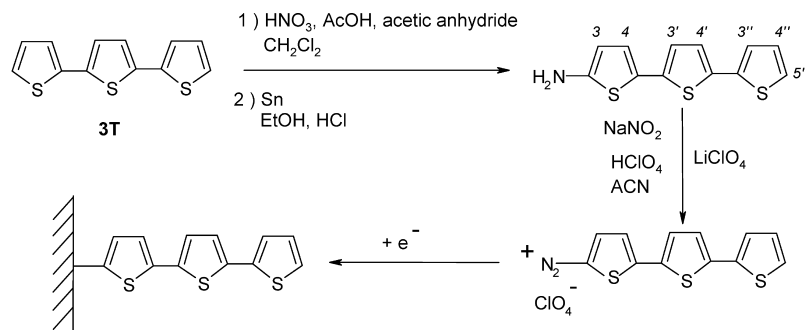
Chemicals. 2,2':5',2''-Terthiophene (denoted 3T) was synthesized according to a published procedure.²⁷ All chemical reagents were used as received. Perchloric acid (HClO₄, 17 M) was purchased from Acros Organics, and sodium nitrite (NaNO₂) from Fluka. Ferrocene (Fc), decamethylferrocene (DmFc), and thianthrene (Th) from Aldrich were used as redox probes. Lithium perchlorate (LiClO₄) from Aldrich was used as the supporting electrolyte at 0.1 M concentration in acetonitrile (ACN).

Synthesis of 2-Amino-5,2':5',2''-terthiophene (NH₂-3T). 2-Aminoterthiophene was synthesized in two steps. The first step is the formation of 2-nitroterthiophene, and the second, the chemical reduction of the latter. 2,2':5',2''-Terthiophene (1.24 g, 5 mmol) was dissolved in dichloromethane (10 mL), then acetic anhydride (10 mL) was added. After the mixture had been cooled to 5 °C a 10:1 mixture of concentrated acetic and nitric acids (2.5 mL) was added. The resulting dark-red solution was stirred 5 min at this temperature. It was then allowed to warm to room temperature and was stirred

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Scheme 1. Two-Step Synthesis of 2-Aminoterthiophene, Followed by in Situ Generation of Diazonium Cation and Its Electrochemical Reduction at an Electrode



overnight. Next, distilled water (60 mL) was added and the mixture stirred for 30 min before filtering. The crude product was collected and recrystallized from dichloromethane/hexane. 2-Nitroterthiophene was obtained as a dark-red powder (0.7 g, 48%). ^1H NMR (200 MHz, DMSO, ppm): δ 8.11 (d, $J = 4.4$ Hz, 1 H; H_3), 7.67 (d, $J = 3.9$ Hz, 1 H; $\text{H}_{3'}$ or $\text{H}_{4'}$), 7.62 (dd, $J = 5.1, 1.0$ Hz, 1 H; $\text{H}_{5''}$), 7.45 (d, $J = 4.4$ Hz, 2 H; $\text{H}_{3''}$ and H_4), 7.39 (dd, $J = 3.9, 1$ H; H_3 or $\text{H}_{4'}$), 7.13 (dd, $J = 5.1, 3.7$ Hz, 1 H; $\text{H}_{4''}$).

2-Nitroterthiophene (0.2 g) was dispersed in absolute ethanol (10 mL), and concentrated HCl (10 mL) was added. Then the temperature was lowered to 15 °C and tin powder (1 g) added. The mixture was allowed to warm to room temperature and was stirred for 36 h. The reaction was followed by TLC (7/3 petrol ether/ethyl acetate) to make sure that all the 2-nitroterthiophene was consumed. Finally, the mixture was filtered and the green solid dispersed with vigorous stirring in ethyl acetate and NaOH (1 M) for at least 1 h. The organic phase was washed with water until neutral, dried over MgSO_4 , and filtered; the solvent was removed by evaporation. Finally, 2-aminoterthiophene (0.13 g, 73%) was obtained as a brownish powder. ^1H NMR (300 MHz, DMSO- d_6 , ppm): δ 7.45 (dd, $J = 5.1, 1.2$ Hz, 1 H; $\text{H}_{5''}$), 7.23 (dd, $J = 3.6, 1.2$ Hz, 1 H; $\text{H}_{3''}$), 7.13 (d, $J = 3.9$ Hz, 1 H; $\text{H}_{3'}$ or $\text{H}_{4'}$), 7.06 (dd, $J = 5.1, 3.6$ Hz, 1 H; $\text{H}_{4''}$), 6.85 (d, $J = 3.6$ Hz, 1 H; H_4), 6.81 (d, $J = 3.9$ Hz, 1 H; H_3 or $\text{H}_{4'}$), 5.91 (s, 2 H; NH_2), 5.83 (d, $J = 3.6$ Hz, 1 H; H_3).

In Situ Preparation of 2-Terthiophenyldiazonium Cation. The diazonium salt was obtained in the electrochemical cell and was not isolated prior to grafting. A solution containing 5 mM NH_2 -3T and 0.1 M LiClO_4 was prepared in acetonitrile. Then, 30 μL of HClO_4 (17 M) was added, followed by 2 equiv of NaNO_2 . Diazonium formation does not happen instantly and because of that the use of only one equivalent yielded to a mixture of diazonium and unreacted aminoterthiophene that can react in diazotation prior to grafting. We have used two equivalents because, with these conditions, better grafting was obtained and because the use of one equivalent yielded to films with pinholes as evidenced using electrochemistry. UV-vis spectrum has evidenced the diazonium formation.

Electrochemical Experiments. A conventional three-electrode cell was used with a platinum wire as auxiliary electrode and a saturated calomel electrode (SCE) (3 M KCl) as reference. The potentials were checked versus the ferrocene/ferrocenium couple, and all potentials were scaled against SCE. Three types of working electrode were used, namely glassy carbon (GC, 3 mm diameter), platinum UME (25 μm diameter), and gold (1 cm^2) for XPS analysis. Prior to use they were polished using decreasing sizes of diamond paste. Before any measurements the solutions were deoxygenated by bubbling argon for 30 min; during the experiment the electrochemical cell remained under argon. The potentiostat was a CHI 660C (CH Instruments, made in U.S.A.), and for the SECM experiments, an instrument with closed-loop piezoelectric motors, CHI 900B (CH Instrument, Austin, TX), was used.

X-ray Photoelectron Spectroscopy. XPS analyses were performed on a modified gold substrate using a VG Scientific

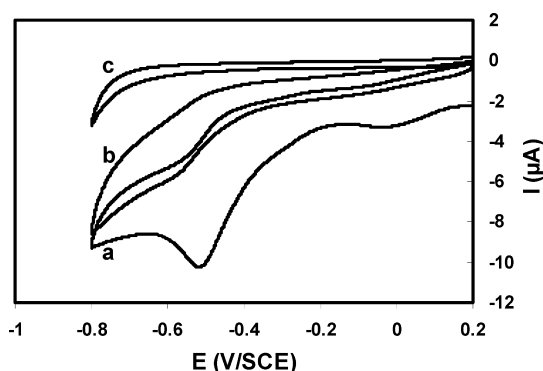


Figure 1. Cyclic voltammograms of 2-terthiophenyldiazonium cation on GC electrode: (a) 1st cycle, (b) 5th cycle, (c) 15th cycle. Scan rate 0.05 V/s.

ESCALAB 250 system equipped with a microfocussed, monochromatic Al KR X-ray source (1486.6 eV) and a magnetic lens which increases the electron acceptance angle and hence the sensitivity. A 650 μm X-ray beam was used at 20 mA \times 15 kV. The spectra were acquired in the constant analyzer energy mode with pass energies of 150 and 40 eV for the survey and the narrow regions, respectively. Charge compensation was achieved with an electron flood gun combined with an argon ion gun. The argon partial pressure in the analysis chamber was 2×10^{-8} mbar. Avantage software, version 2.20 (Thermo Electron), was used for digital acquisition and data processing. Spectra were calibrated by setting the main C1s signal to 285 eV. Surface compositions (in atom %) were determined from the integrated peak areas and the corresponding sensitivity factors corrected for the analyzer transmission.

Results and Discussion

Electrochemical Reduction of 2-Terthiophenyldiazonium on Carbon Electrode. After formation of the 2-terthiophenyldiazonium cation, electrochemical grafting was carried out by cyclic voltammetry. Figure 1 shows the CV of the reduction of the 2-terthiophenyldiazonium cation on a GC electrode.

The CVs recorded under our experimental conditions display two irreversible reduction waves at 0 and -0.5 V/SCE. The main cathodic wave at -0.5 V/SCE is associated to the reduction of diazonium cations. The first reduction wave, at 0 V/SCE, has already been reported, but its nature has still not been clarified;²⁶ it disappears after a few cycles. During subsequent cycles, the CV shows significant decrease in the intensity of the reduction peak at -0.5 V/SCE, and this wave disappears completely after 15 cycles. This behavior can be attributed to the progressive modification of the electrode by the formation of an insulating organic film, which blocks the surface. Similar

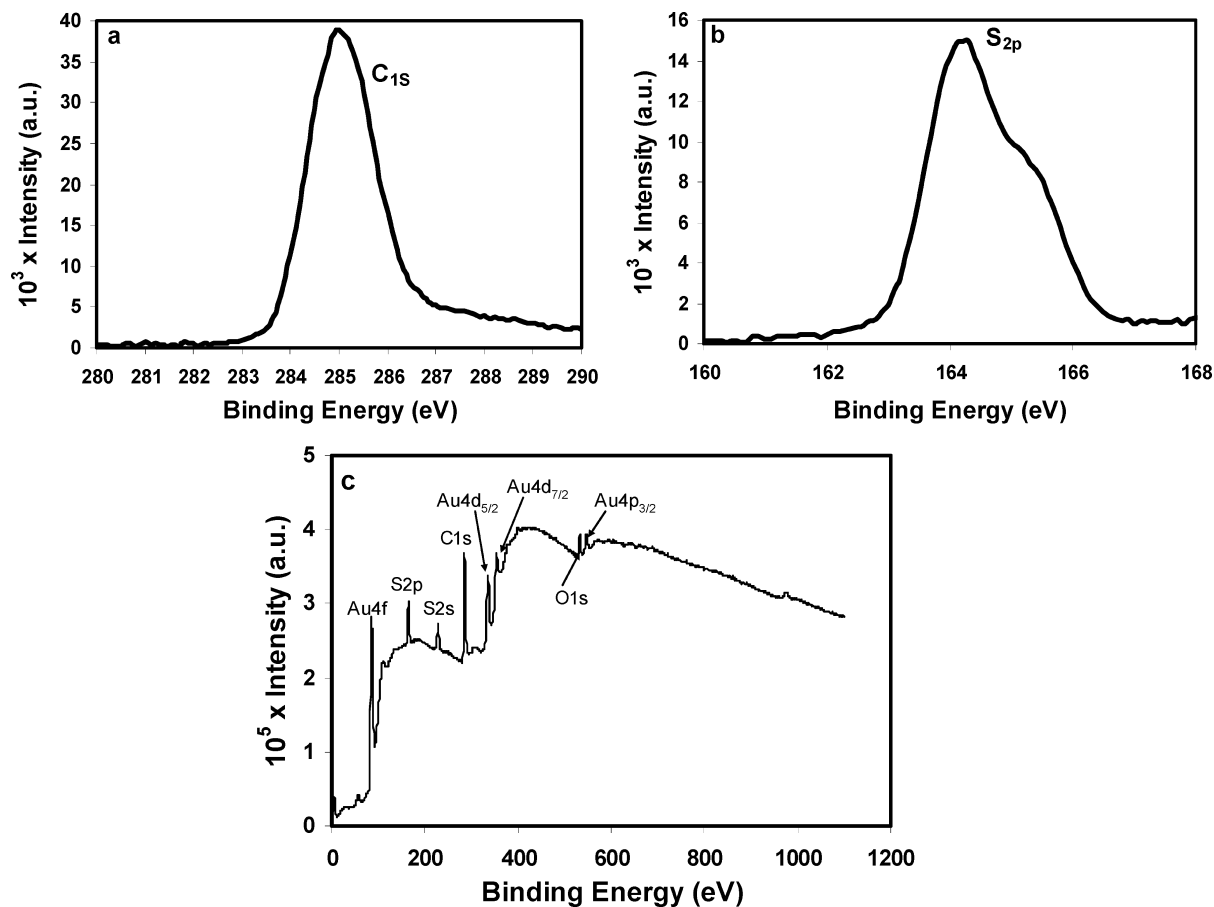


Figure 2. High-resolution XPS spectra of terthiophene-modified gold surface. (a) C_{1s} spectra. (b) S_{2p} spectra. (c) XPS survey spectra of gold modified electrode.

behavior has been observed in the reduction of in situ generated aryldiazonium cations.^{12,28}

XPS Investigation of the Modified Carbon Electrode. A conventional way of characterizing an organic layer attached to an electrode surface is XPS analysis. We used this technique to prove that terthiophene or oligothiophene was attached to a 1 cm^2 gold electrode. Electroreduction of $\text{NH}_2\text{-3T}$ was performed as for the GC electrode. The modified electrode was first sonicated in acetonitrile for 20 min, to remove any weakly adsorbed species. Figure 2 displays the high-resolution XPS spectrum for C_{1s} (Figure 2a) and S_{2p} (Figure 2b) obtained on the modified surface.

Comparison of the XPS spectra before and after electrochemical grafting reveals several major differences. First, the carbon and sulfur signals increase after the reduction of diazonium, in comparison with the bare substrate, which indicates the formation of an organic layer. (The carbon on the gold surface before grafting is attributed to surface contamination.) Figure 2b displays a doublet of S_{2p} with an intensity ratio of 2:1 assigned to $S_{2p_{3/2}}$ and $S_{2p_{1/2}}$, which is in perfect agreement with literature reports.²⁹ This doublet at around 164 eV can be considered as the signature of thiophene sulfur on the modified gold surface and is not seen on the bare electrode. The atomic ratio, C/S , is about 4.1, which suggests that the

observed surface species is derived from thiophene ($C/S = 4$) and that the contribution from contaminants that are initially adsorbed on the gold surface is now negligible. The other interesting feature of the XPS analysis is the absence of a N_{1s} peak at 403.8 eV, corresponding to nitrogen of the diazonium cation.²⁶ No peak corresponding to -N=N- (indicative of an undesired coupling reaction between the diazonium salt and $\text{NH}_2\text{-3T}$) was observed,³⁰ but a weak N_{1s} peak at 400 eV (2 atom %) reveals surface amino groups or reduced nitrogen. Despite the significant changes in the surface compositions resulting from the grafting, the detection of the Au XPS signals, in the survey spectrum (Figure 2c), is an indication of rather thin (<10 nm, which is the analysis depth of XPS). Furthermore, it is interesting to note that the spectrum exhibits intense inelastic backgrounds beyond Au_{4f} , Au_{4d} , and Au_{4p} peaks, whereas it remains constant or decreases beyond C and S signals. The inelastic scattering of photoelectrons from the underlying gold substrate is due to screening of gold, whereas the decrease after the C and S signals confirms that these atoms are located at the extreme surface (note that X-rays penetrate to 1–10 μm but photoelectrons escape from a few nanometers only).³¹ Finally, the XPS results are consistent with the presence of a terthiophene or oligothiophene layer grafted onto the electrode surface. The UV–vis spectrum of the “as grafted” solid film formed on ITO

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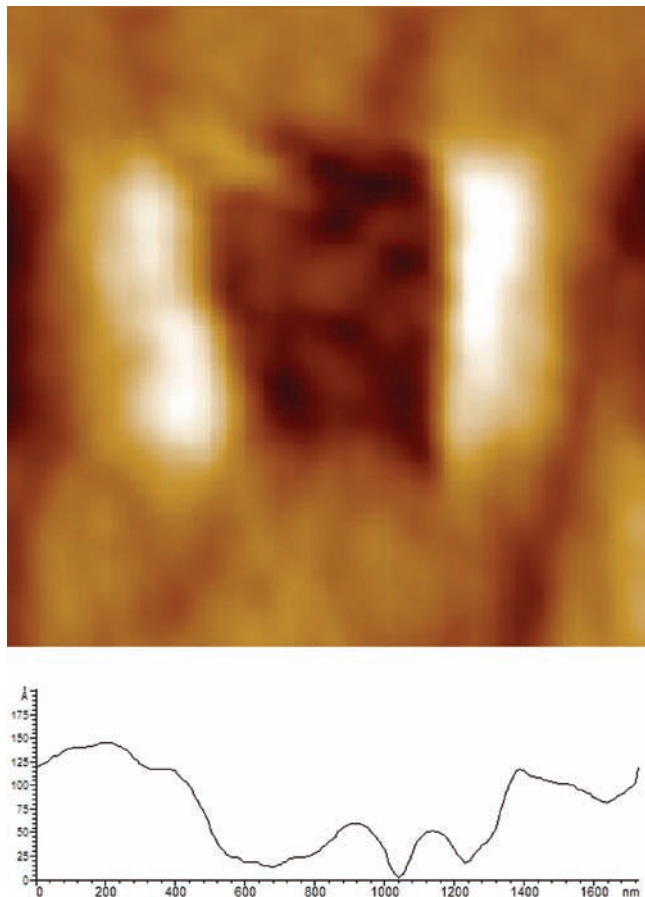


Figure 3. AFM image of 3T modified electrode after scratch experiment with AFM tip in contact mode.

electrodes shows a small UV band with an onset around 500 nm and a maximum at 400 nm. Such values are compatible with sexithiophene or terthiophene subunits grafted on the electrode but not with higher conjugation length oligothiophenes.³² Note that UV-vis failed to give more precise information on this point because the films are too thin for reliable measurements. Precise determination of the effective conjugation length will require other spectroscopic investigations and will be reported elsewhere.

AFM Characterization of the Grafted Layer. The GC-modified surface was investigated using AFM. The film appears homogeneous with no visible pinholes (at the AFM resolution). In addition, scratch experiment made by the AFM tip makes it possible to measure more precisely the film thickness. Figure 3 shows the cross section through the hole generated by the tip. An average thickness of 10 nm is found on GC, whereas smaller thicknesses were found on ITO. These results confirm that the deposited films are of nanometric thicknesses but are not composed of a monolayer of grafted oligothiophenes.

Electrochemical Characterization of the Grafted Layer. Oligothiophenes and terthiophenes are electroactive species and can thus be detected when grafted on a surface using cyclic voltammetry in an electrolyte free of electroactive species. The modified GC electrode was removed from the diazonium solution and was then immersed in a solution containing 0.1 M

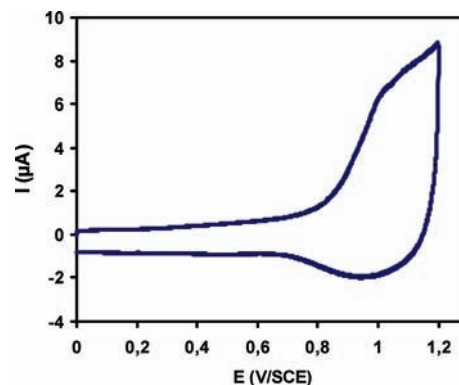


Figure 4. CV of 3T-modified GC electrode in 0.1 M LiClO₄ in ACN. Scan rate 0.1 V/s (first cycle).

LiClO₄ in ACN. The grafted layer is electroactive with one irreversible electrochemical signal adding to the capacitive current of the bare electrode as depicted in Figure 4. It has an onset at 0.8 V/SCE which is similar to that observed when terthiophene is solubilized in 0.1 M LiClO₄ ACN and oxidized on a bare electrode. It can thus be attributed to grafted terthiophene or short oligothiophene. This electrochemical signal corresponds to a total charge of $150 \mu\text{C}\cdot\text{cm}^{-2}$ after sonication. The charge under this electrochemical signal can be used to evaluate the amount of deposited electroactive molecules on the surface and yields to a surface coverage of $1.75 \times 10^{-9} \text{ mol}\cdot\text{cm}^{-2}$ after sonication in the case of one electron oxidation processes. The reported surface coverage on GC substrates⁸ varies in the range of $4\text{--}12 \times 10^{-10} \text{ mol}\cdot\text{cm}^{-2}$ with the theoretical maximum surface coverage for a monolayer on GC surfaces being around $10^{-9} \text{ mol}\cdot\text{cm}^{-2}$. The surface coverage found here clearly indicates that the GC electrode is modified with a few molecular layers rather than with a thick film of oligothiophenes. These results are in agreement with the XPS results. Upon cycling, the terthiophene signal is not stable and decreases in several cases with the concomitant increase of a small reversible signal at 0.5 V/SCE with a close to zero ΔE_p and a charge corresponding to $5 \times 10^{-10} \text{ mol}\cdot\text{cm}^{-2}$. This signal could be attributed to further polymerization. Indeed, terthiophene radical cations are still reactive enough to form higher-length oligothiophenes (such as sexithiophenes or beta-coupled oligomers) even though the oxidation peak of this signal is seen at a lower potential than that of polyterthiophene deposited through the oxidation of terthiophene (note that the reduction peak potential is close to that of polyterthiophene).

Another convenient way of detecting a coating on an electrode surface is to examine it by cyclic voltammetry in an electrolyte solution containing electroactive probes. The modified GC electrode was removed from the diazonium solution, thoroughly rinsed with ACN, and then sonicated. It was then immersed in a solution containing 1 mM of decamethylferrocene (DmFc) as redox probe and 0.1 M LiClO₄ in ACN. The CV obtained is shown in Figure 5.

As expected, the CV of DmFc on a bare GC electrode shows a reversible redox system at a standard potential around -0.2 V/SCE . On the contrary, the 3T-modified GC electrode does not show any activity at the potential expected for the DmFc redox couple. This first result indicates that the electroreduction of 2-terthiophenyldiazonium changes the electrode interface. Furthermore, it can be considered as proof that there is a densely packed organic layer which acts as a barrier against electron transfer from DmFc, at least at the expected redox potential.

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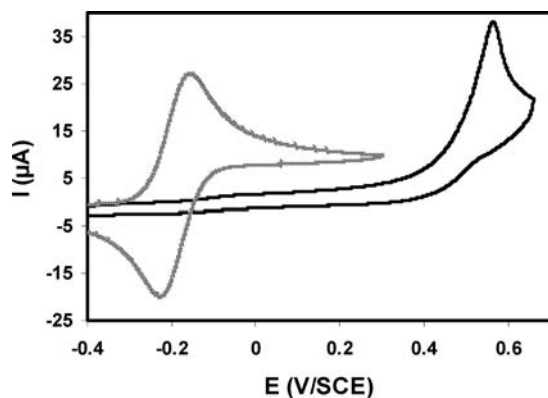


Figure 5. CV of 3T-modified GC electrode in 1 mM DmFc and 0.1 M LiClO₄ in ACN. Scan rate 0.05 V/s. Gray line: bare GC electrode; black line: 3T-modified GC electrode.

However, upon scanning to more positive potentials, an irreversible oxidation wave appears at around 0.6 V/SCE. This wave is attributed to the oxidation of DmFc even though no peak for DmFc⁺ reduction (even at very cathodic polarization) can be observed during the reverse potential scan. Diode-like behavior toward DmFc, with current flowing in only one direction, is thus obtained. Similar behavior has been obtained by our group on bithiophene phenyl grafted onto a GC electrode,³³ and we have shown that, contrary to the usual interpretation of such effects, based on an EC_{cat} mechanism, this response can be explained by assuming that these organic electrodes switch reversibly between conducting and totally insulating states. The positive shift of the oxidation potential can thus be ascribed to the electrochemical properties of the coating, which behaves as a conductive switch at a potential close to 0.5 V/SCE. Thus, the 3T layer can be considered as insulating for potentials less negative than 0.5 V/SCE, giving no DmFc oxidation signal at -0.2 V, and conducting for potentials more positive than 0.5 V/SCE, giving this shifted oxidation signal. In addition, the conductive switch of the 3T-modified electrode explains the disappearance of the reverse reaction. Indeed, during the reverse scan the layer switches back from conducting to insulating, which blocks electroreduction of the electrogenerated DmFc⁺ above the modified electrode. Note that these experiments demonstrate that the conductive switch is reversible (on the time scale investigated in this study).

In order to confirm this mechanism and to get more information about the intrinsic electrochemical properties of the attached layer, other redox probes were used: ferrocene (Fc), $E^\circ = 0.3$ V/SCE, and thianthrene (Th), $E^\circ = 1.2$ V/SCE. Figure 6 shows the CVs obtained on bare and modified GC electrodes in the presence of Fc (Figure 6a) and Th (Figure 6b) as redox couples.

When Fc is the redox probe, the CV on the modified GC electrode does not show any signal of ferrocene at the redox potential obtained on a bare electrode. Scanning to a more positive potential shows an irreversible wave at around 0.65 V/SCE, attributed to the oxidation of Fc. In this case, reduction of electrogenerated Fc⁺ is not observed, since the reverse reaction occurs at a potential where the organic layer returns to its insulating state. However, in the case of the Th⁺/Th redox

couple a reversible redox wave is obtained on the modified electrode, and no shift of potential is observed compared to the bare electrode (Figure 6b). The organic layer appears to be completely “transparent” for this probe (on the time scale investigated) and clearly demonstrates the switching of the layer conductivity (note that these observations are not compatible with an alternative EC_{cat} mechanism with electroactive immobilized centers characterized by a single redox potential but remains compatible with an EC mechanism in which the layer has several redox sites with different oxidation potentials). The modified electrode acts as a conducting material, since the standard redox potential of the Th⁺/Th couple is more positive than the intrinsic potential of the attached organic layer switch potential. After the response of the modified electrode in the presence of Th had been recorded, the electrode was immersed in a solution containing Fc or DmFc, and behavior similar to that presented in Figure 5 or Figure 6a was still observed. These experiments prove that the layer is still present after scanning the potential to 1.4 V in the Th solution, indicating its high stability under these conditions. Finally, this study demonstrates that it is possible to graft a heteroaromatic group on an electrode, even in the absence of phenyl groups, by the electrochemical reduction of a diazonium cation.

Electrochemical Grafting and Characterization on Platinum UME. One of the advantages of electrografting organic layers by reducing a diazonium cation is that it is possible to perform such a reaction on various electrode materials.^{14,15,17,16,20} Electrochemical reduction of 2-terthiophenyldiazonium cation on a platinum ultramicroelectrode was investigated. Modifying an UME by the reduction of diazoniums has been already described and was found to be suitable for several applications in analysis and nanotechnology.^{34,35}

A platinum UME was treated under conditions similar to those described for the GC electrode, the 2-terthiophenyldiazonium cation being generated in the electrochemical cell, and then reduced by cyclic voltammetry. The recorded CV is similar to that presented in Figure 1. An irreversible reduction wave which appears at around -0.4 V/SCE is attributed to reduction of the diazonium in the vicinity of the UME. Note that no steady-state current is obtained; this indicates that the electroreduction is not diffusion-limited, in agreement with results obtained for the electroreduction of nitrophenyldiazonium salt in acetonitrile on a similar UME.³⁵ Upon successive cycles, this wave disappears progressively. To see whether there was an organic layer on the Pt UME its electrochemical response was examined in a test solution containing redox probes. The UME was thoroughly rinsed and sonicated in ACN, then immersed in the test solution. The CV was recorded using the same three redox probes DmFc, Fc, and Th, as for the GC electrode (Figure 7).

All the CVs for bare or modified Pt UME show a steady-state voltammogram, which indicates that the signal recorded on the modified UME is due to the diffusion of the redox species from the solution to the electrode. Two different situations arise, depending on the redox probe. In the case of DmFc and Fc, the modified electrode does not show any signal at the standard redox potential expected by comparison with bare Pt UME (Figure 7a). However, a steady-state current is observed around 0.6 V/SCE. This result confirms the conductance switch of the

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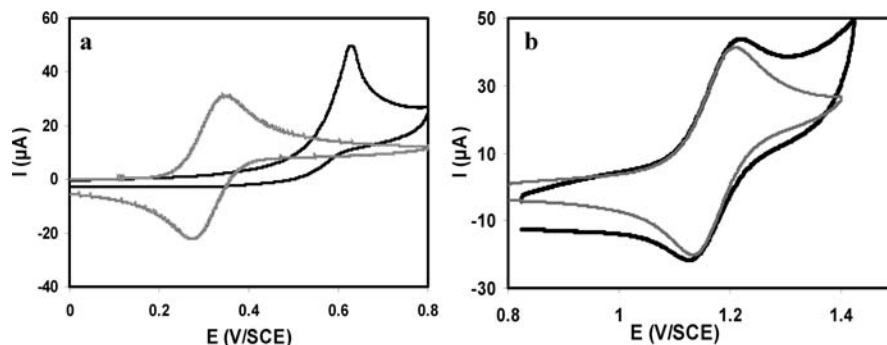


Figure 6. CV of bare (gray line) and 3T-modified GC electrode (black line) in 0.1 M LiClO₄ in ACN: (a) in presence of 1 mM ferrocene, (b) in presence of 1 mM thianthrene. Scan rate 0.05 V/s.

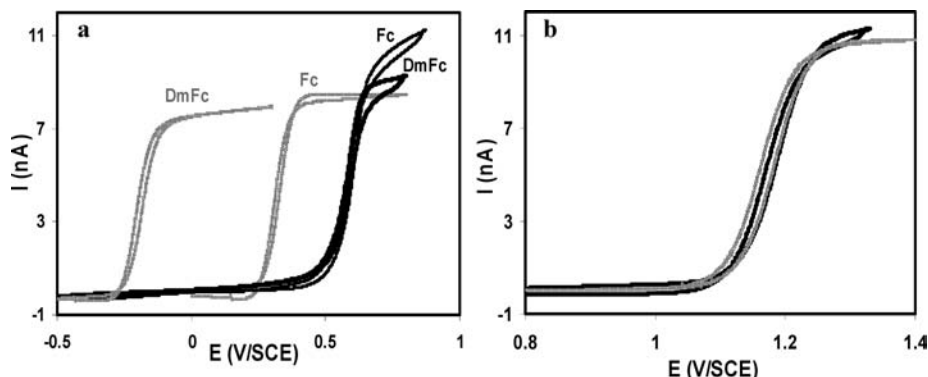
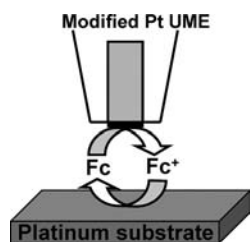


Figure 7. Steady-state CV on bare (gray line) and 3T-modified Pt UME (25 μm diameter) (black line) in 0.1 M LiClO₄ in ACN: (a) DmFc and Fc, (b) Th. scan rate 0.05 V/s.

Scheme 2. Principle of SECM in Feedback Mode When a Modified Pt UME Approaches a Conducting Substrate



modified layer. Indeed, it can be considered as insulating for potentials less negative than 0.5 V/SCE, which explains why oxidation signals for DmFc and Fc at -0.2 and 0.3 V are not observed, but conducting for potentials more positive than 0.5 V/SCE, which gives the observed steady-state current at around 0.6 V/SCE for both redox probes. Note also that these results indicate that the coating is free of pinholes. On the contrary, with Th (standard potential around 1.2 V/SCE) similar steady-state CVs are obtained above bare and modified Pt UME, as shown in Figure 7b. This result indicates that the attached layer acts as a conducting electrode without any barrier effect. All these results are in perfect agreement with the previous results obtained on a GC electrode, confirm the grafting of 3T or oligothiophene layers on the platinum UME, and indicate that a switchable UME has been obtained.

Scanning electrochemical microscopy (SECM) experiments using this switchable UME were finally performed. The basic principle of SECM operating in the feedback mode is presented in Scheme 2.

SECM experiments were run in an ACN solution of 0.1 M LiClO₄ and 1 mM Fc. The modified Pt UME was used as probe

tip, and its potential was held at 0.9 V/SCE to generate Fc⁺ while the tip was brought up to the platinum substrate and the approach curve recorded. One has to note that, if the tip potential was set at the expected redox potential of Fc, 0.4 V/SCE, no Faradaic current is observed, because the organic layer is insulating at this potential. The SECM experiments were possible only when the tip potential was held at a sufficiently high potential in order to switch the layer to its conductive state. At this potential, the backward reduction reaction is completely inhibited, and in a sense, the layer acts as a filter toward the probe standard potential which may prove useful for mechanistic studies of electrochemical process occurring with different driving forces, especially in case of ECE (multiple electron transfer)

The approach curves were plotted as the normalized current, I , versus the normalized distance, $L = d/a$, where d is the tip-substrate distance, as shown in Figure 8.

For $L > 3$ the normalized current is close to unity, showing the absence of any interaction between the electrogenerated species at the modified UME and the substrate. In addition, this value indicates that the steady-state current is obtained when the 3T-modified UME is used, which is in agreement with the CV result described above (Figure 7a). For $L < 3$ one observes an enhancement of the current and positive feedback. This behavior means that the mediator, Fc, is regenerated at the Pt substrate. The experimental approach curve obtained with the modified UME is similar to the theoretical curve expected for a conducting substrate under diffusion control. Moreover, positive feedback confirms (i) that the electrogenerated species, Fc⁺, at the tip is stable and diffuses to the substrate where it undergoes the reverse reaction and (ii) that the layer is stable

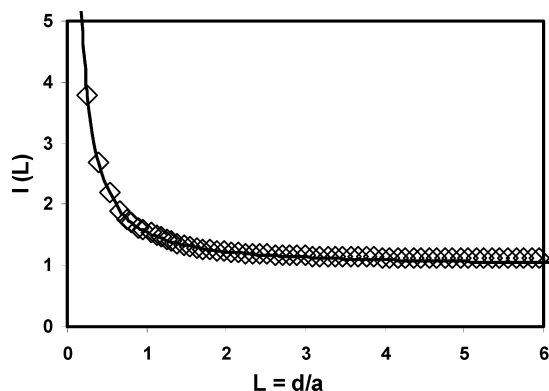


Figure 8. (\diamond) SECM approach curve obtained with 3T-modified Pt UME (radius $a = 12.5 \mu\text{m}$) onto a platinum substrate in 1 mM Fc and 0.1 M LiClO_4 in ACN. Solid line is the theoretical curve for totally conducting substrate.

in its conductive state under the experimental conditions used. This result shows clearly that it is possible to record the SECM approach curve using the switchable organic layer attached to the UME. One has to note that, on the contrary, if the substrate and not the UME is modified, the approach curve obtained with Fc exhibits total negative feedback, and there is no regeneration of Fc at the modified substrate, which is consistent with the CV results.

Conclusions

A new diazonium cation, without phenyl groups, has been generated directly, in an electrochemical cell, from an amino-heteroaromatic compound; its electroreduction is similar to that observed for the phenyldiazonium (or substituted phenyl) derivative and strongly suggests that grafting to the electrode material occurs. The presence of organic layers on a modified gold surface was established by XPS analysis: 3T or oligothiophene moieties are clearly attached to the electrode. The film cannot be more than 20 nm thick. The coating is electroactive at a potential close to that of terthiophene and oligothiophene in solution. Grafting on GC electrodes was also evidenced by

cyclic voltammetry in solutions containing redox probes. The attached layer acts as barrier for a redox couple with a standard potential below 0.5 V/SCE and shifts the oxidation wave of the probe to a more positive potential; in this case diode-like behavior is observed. On the contrary, for probes with a more positive redox potential, the attached layer is conducting, and no barrier effect is observed (at the time scale investigated). Electrochemical grafting to a platinum UME gives organic layers which appear to be transparent toward Th, whereas they shift the steady-state wave for Fc and DmFc to values similar to those given above for GC. This result confirms that an oligothiophene layer is grafted onto the UME and its conductance switches at around 0.5 V/SCE. Furthermore, it is possible to do SECM measurements on the switchable organic-modified UME using Fc as mediator but at a tip potential of 0.9 V/SCE, in order to maintain the layer in its conductive state. In conclusion, ultrathin layer junctions based on conjugated oligomers have been obtained with reversible *on/off switching* capabilities controlled by the redox state of the oligomer. In view of previous work, it is likely that the oligomers are covalently bonded to the electrode, and therefore, this method may allow better control of the metal/molecule interface than other oligothiophene deposition methods. We anticipate that such layers will be of wide interest in plastic and molecular electronics and for redox-gated transport experiments in metal/molecule/metal systems. It may also prove useful for mechanistic studies when filtering the backward reaction is useful. Furthermore, it should also be possible to extend this procedure for the controlled preparation of modified surfaces and structured interfaces based on the grafting of a variety of heteroaromatic groups other than the commonly used phenyl groups.

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