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Formation of Mixed Organic Layers by Stepwise Electrochemical Reduction of Diazonium Compounds

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ABSTRACT: This work describes the formation of a mixed organic layer covalently attached to a carbon electrode. The strategy adopted is based on two successive electrochemical reductions of diazonium salts. First, bithiophene phenyl (BTB) diazonium salt is reduced using host/guest complexation in a water/cyclodextrin (β -CD) solution. The resulting layer consists of grafted BTB oligomers and cyclodextrin that can be removed from the surface. The electrochemical response of several outer-sphere redox probes on such BTB/CD electrodes is close to that of a diode, thanks to the easily p-dopable oligo(BTB) moieties. When CD is removed from the surface, pinholes are created and this diode like behavior is lost. Following this, nitrophenyl (NP) diazonium is reduced to graft a second component. Electrochemical study shows that upon grafting NP insulating moieties, the diode-like behavior of the layer is restored which demonstrates that NP is grafted predominately in the empty spaces generated by β -CD desorption. As a result, a mixed BTB/NP organic layer covalently attached to a carbon electrode is obtained using a stepwise electrochemical reduction of two diazonium compounds.

The formation of modified surfaces with well ordered structures have been shown to be particularly useful for applications ranging from molecular electronics to chemical or biochemical sensors.^{1,2} A number of methods have been proposed to decorate the electrode surface using various compounds. Among these, self-assembled monolayer adsorption of organic thiols on a gold substrate,³ surface silanization based on organosilane derivatives⁴ and electroreduction of diazonium salts on various materials⁵ are the most popular. Thiolate and organosilane have been successfully used to build mixed organic layer SAMs. This was mainly performed in a one-step procedure by exposing the substrate to a solution containing two thiols,^{3b,6} but some approaches using a two-step procedure have also been reported.⁷

In the field of molecular electronics, there have recently been important developments in metal/molecule/metal device fabrication techniques and in experimental approaches allowing the manipulation and the electronic investigation of single or small numbers of molecules. The favorite approach is again based on molecular self-assembly using a uniform or mixed organic layer combined with scanning probe microscopy.⁸ The deposition of a top electrode by various techniques is also used to generate large-area molecular junctions.⁹ In both cases, three important questions are raised: (i) what is the impact of the

metal/molecule bond on the device, (ii) what is the impact of lateral electron hopping, and (iii) to what extent is the control and/or the modulation of this lateral “cross talk” between the molecules, an important parameter for the design of molecular electronic devices.

In this context, new methods for generating mixed layers of molecules covalently grafted on a surface through various chemical bonds are important. Diazonium electrochemistry allows the covalent attachment of various functional groups to a large variety of materials.⁵ As a consequence, the layers are much more robust, less organized but much less labile than SAMs on gold. This technique is thus complementary to that based on thiol adsorption. Electrografting using mixtures of diazonium salts leads to a modified surface with a mixed organic layer, but the final composition is hard to predict due to the high and unselective reactivity of the aryl radicals generated.¹⁰ Overall, it appears that the formation of an organic layer based on one component is straightforward, while adjusting the surface morphology and composition of a mixed organic layer using diazonium electroreduction in a one-step procedure is complicated.

To overcome this drawback, other approaches based on stepwise deposition have been proposed.¹¹ However, for diazonium electrochemistry such a strategy is limited. Indeed, the electrogenerated aryl radical, for the second component, is highly reactive and may graft over the primary layer. This method has been used for the functionalization at the submicrometer scale of patterned surfaces.¹² Recently, the electrografting of diazonium combined with protection–deprotection methods has been proposed for the fabrication of mixed organic layers.^{13,14} In this connection, our group has demonstrated that bithiophene phenyl (BTB) can be electrografted in the presence of cyclodextrin (β -CD) in aqueous solution. As a result, a mixed layer is obtained consisting of covalently attached bithiophene phenyl oligomers and adsorbed cyclodextrin, which can be easily desorbed, creating holes on the nanometer scale.¹⁵

In this work, we propose to use the two-step electrochemical reduction of diazonium salts to build a mixed organic layer covalently attached to a carbon electrode. We take advantage of the free space left after β -CD removal from the BTB generated in the presence of β -CD, and the unique electrochemical properties of the oligo(BTB) layer to perform the second graft. This was achieved by using nitrophenyl diazonium (NPD), which is easily detected by electrochemical methods after grafting.¹⁶ The modified mixed surface was characterized by

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electrochemistry, to probe the attached NP groups, and also in the presence of a redox couple, in order to evaluate the electron transfer behavior across the mixed layer.

Figure 1a shows the electrografting of oligo(BTB) in β -CD aqueous solution using host/guest complexation followed by

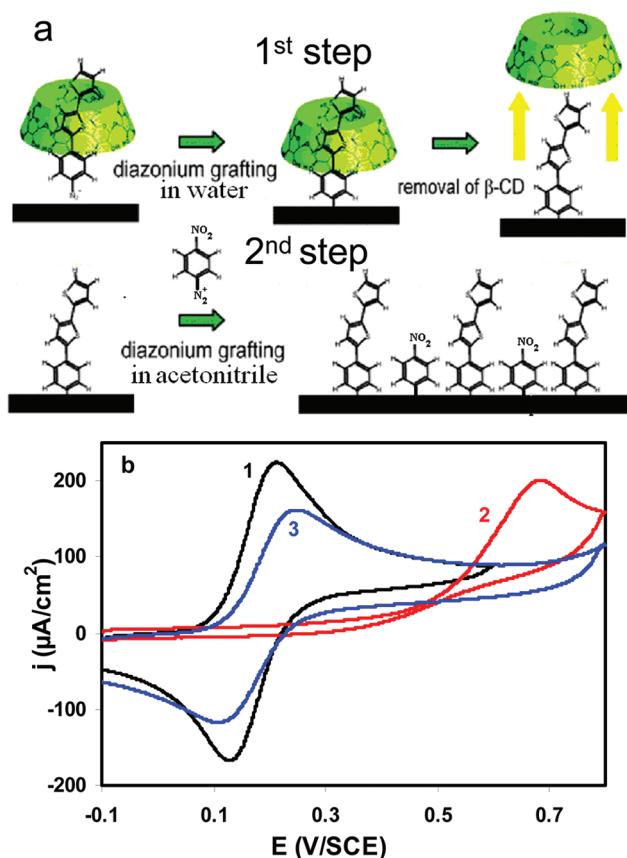


Figure 1. (a) Scheme showing the two-step grafting procedure. (b) Cyclic voltammograms in 1 mM FcMeOH + 0.1 M LiClO₄ in water on a bare carbon electrode (1) on a BTB/ β -CD before (2) and after β -CD desorption (3). Scan rate: 100 mV s⁻¹.

electrochemical removal of the adsorbed β -CD. Details for the elaboration, the cleaning and the characterization of such a surface have been reported.¹⁵ Figure 1b compares the electrochemical response of ferrocene methanol (FcMeOH) on bare carbon and on a BTB/ β -CD-modified carbon electrode, before and after β -CD desorption.

For the BTB/ β -CD electrode there is no FcMeOH signal at the expected potential (red curve). However, when scanning is continued to more positive potentials, the current increases dramatically and an irreversible wave is observed with an oxidation peak at 0.6 V. Such behavior is related to the electroactivity of the grafted layer, which acts as a dopable organic semiconductive material and switches from an insulating state to a conductive state above a potential threshold at around 0.5 V/SCE. Similar behavior has been reported for a BTB-modified electrode generated in acetonitrile (without cyclodextrins).¹⁷ When host/guest complexation is used in water, the modified surface consists of grafted BTB and β -CD; the latter can be removed from the surface. Indeed, after β -CD desorption the FcMeOH signal is similar to that recorded on a bare electrode but with a lower peak current and higher peak-to-peak potential separation (blue curve). Such behavior is

similar to a partially blocked electrode in a case of low coverage and/or in the presence of pinholes. This change in the electrochemical response is due to the free space left after β -CD desorption. The peak shape behavior indicates that there are no individual microdomains and that the holes generated are sufficiently close to ensure electronic communication between them. At this stage, the surface is partially modified by oligo(BTB) groups (labeled "BTB/holes") and can be used to perform the second functionalization step, as sketched in Figure 1a.

Figure 2a shows the electrochemical reduction of NPD on a bare electrode, on BTB/holes, and on a BTB-modified carbon

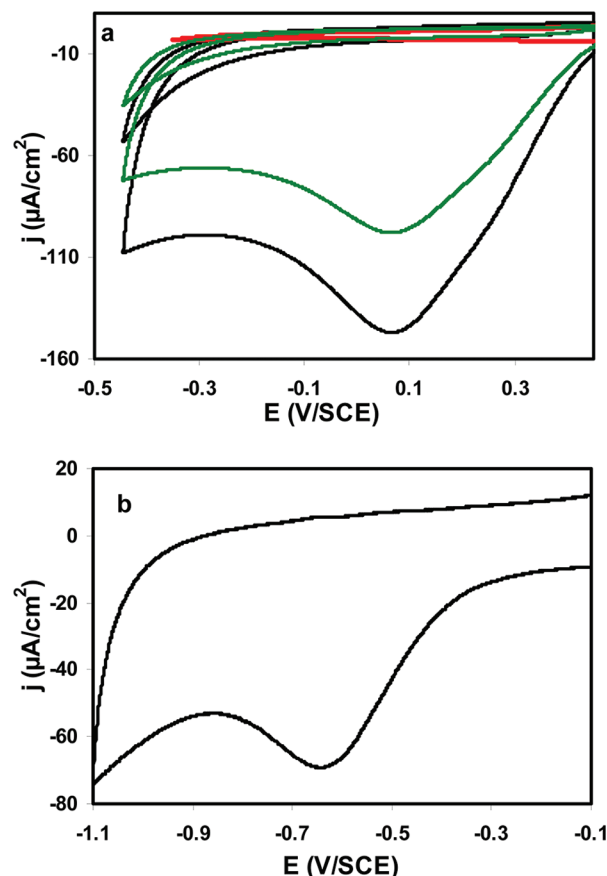


Figure 2. (a) CVs corresponding to the electroreduction of NPD onto a bare carbon electrode (black), on BTB/holes (green), and on a BTB-modified electrode (red). (b) Characterization of BTB/NP-modified carbon electrode in 0.1 M H₂SO₄. Scan rate 0.1 V s⁻¹.

electrode. Cyclic voltammograms of a bare glassy carbon electrode (black curve) and a BTB/holes electrode (green curve) in the presence of NPD show an irreversible cathodic wave at 0.1 V, corresponding to the reduction of the NPD and the subsequent grafting of NP groups at the surface. Upon a second scan the irreversible wave disappears and cannot be recovered upon further scans. This behavior clearly demonstrates that grafting occurs on the BTB/holes electrode. The peak current corresponding to the reduction of diazonium cations on the BTB/holes electrode is only 65% of that for a bare electrode. This variation reflects a lower electroactive surface area due to the presence of BTB oligomers. However, it is not possible to evaluate the surface area from cyclic voltammetry data recorded upon grafting, because the cathodic current depends on the grafting efficiency.

On the contrary, when the electrochemical reduction of NPD is performed on a BTB-modified surface (Figure 2a, red curve), no peak corresponding to diazonium reduction is observed, which rules out the possibility of generating the NP radical above the BTB molecules. This result is due to the BTB layers acting as diodes and preventing reduction processes below 0.5 V. At this stage, the attachment of NP groups on the BTB/holes electrode may occur predominately on the free carbon area, but the possibility of overgrafting on BTB molecules cannot be excluded (see below).

The electrochemical response of the BTB/NP electrode in acidic media (Figure 2b) has been studied. It reveals the presence of an irreversible reduction wave at -0.6 V/SCE corresponding to nitrobenzene reduction. The presence of this signal indicates that NPs are immobilized on the electrode. During the reverse scan a reversible system (attributed to the redox couple NHOH/NO) is observed around 0.2 V/SCE (data not shown).¹⁸ In addition, the surface concentration of NP groups, calculated by integration of the cathodic peak and also the oxidation peak of the NHOH/NO system, is found to be between 1×10^{-10} and 2×10^{-10} $\text{mol}\cdot\text{cm}^{-2}$ (from 10 independent experiments). This value has to be compared with the surface concentration of NP grafted on a bare carbon electrode under similar conditions, around 2×10^{-9} $\text{mol}\cdot\text{cm}^{-2}$. In the case of BTB/NP the surface concentration of NP groups is 10 times smaller than that for uniform NP layers. All these observations strongly suggest the preferential grafting of the NP groups on the free carbon area of the BTB/holes surface rather than overgrafting on BTB oligomers. As a result, mixed organic layers consisting of BTB and NP groups have probably been obtained.

Another convenient electrochemical method for the characterization of the layer is to evaluate the electrochemical response on the modified electrode of a reversible redox probe in solution. Figure 3a shows the cyclic voltammetry of the BTB/NP-modified surface in electrolytic solution containing FcMeOH (green curve). For comparison the response of FcMeOH on the oligo(BTB)/hole electrodes is presented (blue curve). For the BTB/NP-modified electrode, the expected electrochemical signal, ~ 0.2 V/SCE, corresponding to the FcMeOH redox process, has completely disappeared. This result has to be compared with the response of the BTB/holes electrode (blue curve). Indeed, before NP grafting the CV of FcMeOH shows a reversible signal at the expected potential, due to electron transfer from the electrode to the solution through the holes (see Figure 3b left). However, after NP grafting the electrochemical behavior of FcMeOH has been changed, indicating a variation of the electrode interface. The absence of the electrochemical signal at 0.2 V/SCE can be considered as a proof that there is a new insulating organic layer which acts as a barrier against electron transfer from FcMeOH in this potential range. In addition, upon scanning to more positive potentials, an irreversible oxidation wave appears at around 0.7 V/SCE. This wave is attributed to the oxidation of FcMeOH on oligo(BTB) molecules in the layer. In other words, the diode-like response lost after β -CD desorption is recovered in the mixed BTB/NP layer. This behavior is similar to that found for BTB/ β -CD and BTB layers toward FcMeOH.^{15,17}

This result clearly indicates that the holes left by β -CD desorption are occupied by an insulating or a poorly conductive material, as it is in the case of NP groups (see Figure 3b right). In this case the NP groups grafted on the free carbon spaces

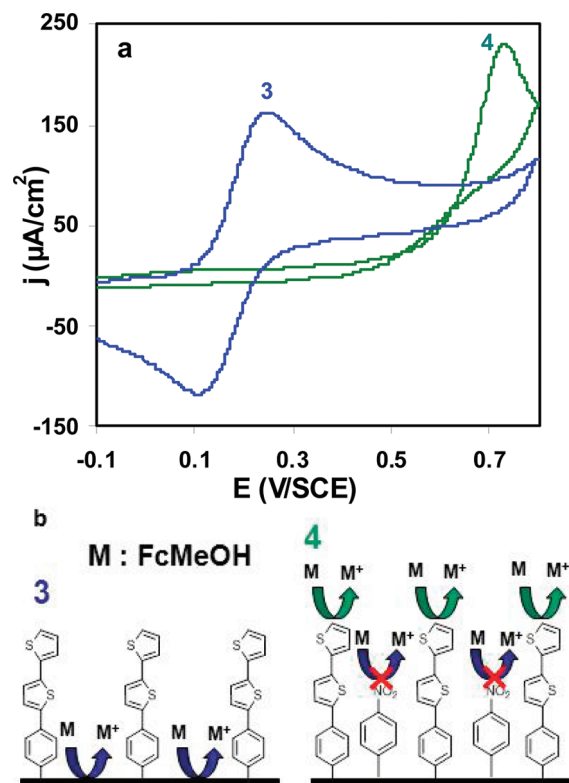


Figure 3. (a) Cyclic voltammograms in 1 mM FcMeOH on BTB/holes (blue) and on BTB/NP (green). Scan rate: 100 mV s^{-1} . (b) Scheme illustrating FcMeOH oxidation on BTB/holes and BTB/NP-modified electrode.

block electron transfer from the electrode to FcMeOH. Otherwise, FcMeOH would be oxidized on these sites, and its response would be similar to that observed on the BTB/holes electrode. Moreover, the magnitude of the current observed with the BTB/NP layer is similar to that recorded before β -CD desorption, indicating that (i) the number of electroactive BTB oligomers has not drastically changed upon NP grafting and (ii) NP is grafted mainly in the nanometer-scale holes allowing communication between the adjacent electroactive oligo(BTB) moieties to behave as a uniform electrode at the investigated scan rates (diffusion layers above individual BTBs overlapping). The recovery of diode behavior for the BTB/NP layer excludes the possibility that the NP groups are overgrafted on BTB molecules. It clearly shows that the electroactivity of the BTB molecules in the BTB/NP layers remains similar to that in a pure BTB layer. In addition, a similar thickness, around 5 nm , was found by AFM scratching experiments on the BTB/holes and on BTB/NP-modified electrodes. All these results suggest that NP groups are predominately attached to the free carbon area generated after β -CD desorption, leading to the formation of a mixed layer consisting of grafted oligo(BTB) and oligo(NP) moieties. This mixed layer still acts as a dopable organic semiconductive material and switches from an insulating state to a conductive state above a potential threshold, despite less lateral electron hopping and “cross talk” between the molecules in the layer.

In summary, this study shows that a mixed BTB/NP layer can be generated on a carbon surface using a stepwise procedure based on two successive electrograftings. In a first step, BTB diazonium salt is grafted in water/ β -CD using host–guest complexation, followed by β -CD desorption. This step

generates a BTB/holes layer with nanometric holes. In a second step, the holes are selectively filled by electrografting the NP diazonium salt, leading to a mixed NP/BTB coating on the carbon electrode. An exciting result is that, after grafting an insulating material (NP moieties), the BTB/NP layer recovers the diode-like behavior associated with the easily p-dopable semiconducting properties and the conductance switch of the grafted oligo(BTB) moieties. This approach, which leads to ultrathin mixed organic layers covalently attached to the surface, may constitute a very interesting route for the generation of novel electroactive multifunctional coatings. Such dilution may compete with and complement the well-known mixed alkyl thiols/gold SAM coatings in many applications. Changing the distribution and the lateral interaction between the immobilized functional molecules could, for instance, be used in molecular electronics to investigate memory effects and lateral electron hopping as against stochastic switching in metal/molecule/metal junctions.

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Notes

The authors declare no competing financial interest.

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