

Derivatization of Carbon Surfaces by Anodic Oxidation of Arylacetates. Electrochemical Manipulation of the Grafted Films

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Received October 16, 1996[®]

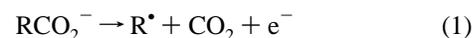
Abstract: Electrochemical oxidation of the corresponding carboxylates (Kolbe reaction) offers a simple and efficient means to solidly attach a monolayer of arylmethyl groups on carbon surfaces. The starting molecules are easily accessible, and the presence of appropriate substituents on the phenyl rings makes this type of derivatization a convenient starting point for further chemical modifications. The extent of the surface modification can be followed by cyclic voltammetry as a function of the number of successive potential cycles. The presence of the groups on the surface, their arrangement, and their concentration are determined by the same technique as well as by X-ray photoelectron spectroscopy and scanning electron tunneling microscopy after transfer of the derivatized electrode into a pure electrolyte solution. The fact that reductive and oxidative cyclic voltammograms of the derivatized electrodes can be obtained demonstrates that the grafted groups are in electrical contact with the electrode by means of electron hopping to or from the aryl moieties they contain. After the electrode has been passivated at the potential whereby anodic oxidation occurs, a second, more positive wave appears. Oxidation at the potential of this second wave triggers a further grafting process leading to a denser film. Electrochemical manipulations allow not only the attachment of electroactive films on the carbon surface but also their erasing by setting the electrode potential at a value where the attached groups are oxidized.

Derivatization of carbon surfaces is an important tool in the design of carbon composite materials.¹ It may also have various applications in the field of sensors if the carbon substrate may be used as an electrode. Another conceivable application of attaching molecules onto a conducting surface is to help transforming the rich potentialities offered by molecular engineering into actual devices.

The standard methods used for modifying the carbon surface involve vigorous oxidation processes leading to the formation of carboxylic, quinonic, ketonic, or hydroxylic groups on the surface² which can then be coupled with the molecule to be attached. These procedures lead to the formation of oxygenated functionalities on the carbon surface whose nature and number are difficult to identify and control. More recently two electrochemical procedures for derivatizing carbon surfaces, one anodic and the other cathodic, have been described. The former consists in the electrochemical oxidation of amines leading to the formation of surface carbon–nitrogen bonds.³ The latter involves the electrochemical reduction of aryl diazonium salts yielding the corresponding aryl radical which then combines covalently with the carbon surface.⁴

We have found that the anodic oxidation of carboxylates, RCO_2^- , on carbon electrodes leads to solid attachment of the

R radical onto the carbon surface. The electrochemical oxidation of carboxylates, the Kolbe reaction,⁵ is the oldest electro-organic reaction. It has received numerous synthetic applications.⁶ In a first stage, the carboxylate ion transfers one electron to the electrode, giving rise to carbon dioxide and to the R radical:



Whether electron transfer and bond breaking are concerted or whether the reaction involves the RCO_2^\bullet radical as an intermediate has long been debated.^{6d,7–9}

One of the main interests of binding molecules to a surface lies in the possibility to further extend the attached molecular structure by inclusion of preselected functionalities. This is the reason why we have focused attention on arylmethyl carboxy-

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Chart 1

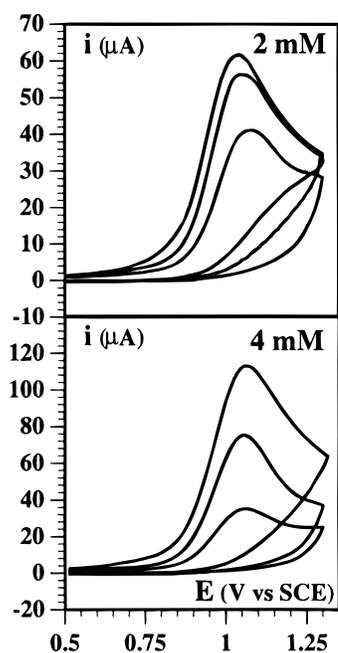
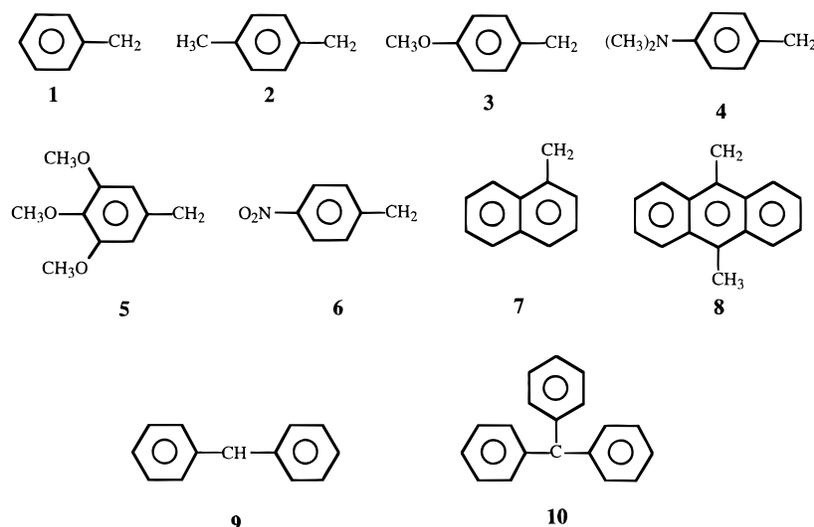


Figure 1. Repetitive cyclic voltammety of **1** in acetonitrile + 0.1 M *n*-Bu₄N(PF₆) at a glassy carbon electrode. Scan rate: 0.2 V/s. The solution is agitated between each of the successive cycles.

lates since the presence of an appropriate substituent on the aryl moiety allows the grafting of a large variety of functionalities onto the layer attached to the carbon surface. The various arylmethyl groups contained in the carboxylates that were investigated are shown in Chart 1.

Results and Discussion

Most of the experiments were carried out in acetonitrile in the presence of 0.1 M *n*-NBu₄PF₆ at a glassy carbon electrode. However, highly oriented pyrolytic graphite (HOPG), with the basal plane exposed to the solution, was used for characterization of the electrode coatings by scanning electron tunneling microscopy (STM).

First Grafting Process. A first indication of the derivatization of the electrode surface upon anodic oxidation of the carboxylate ions is given by repetitive cyclic voltammety in the potential range where they are oxidized. Figure 1 shows a typical example of the self-inhibition phenomenon triggered by oxidation the carboxylate ion. In each cycle, an irreversible

cyclic voltammogram is observed in agreement with the fact that the anodic reaction is itself irreversible as depicted in eq 1. The anodic peak decreases steadily with the number of cycles until it disappears completely. With **1**, at a scan rate of 0.2 V/s, the anodic current disappears after 13 cycles for a concentration of 2 mM and after nine cycles for a concentration of 4 mM. It should be emphasized that, in these experiments, the solution is rehomogenized between two successive cycles by argon bubbling. Therefore, this phenomenon should not be confused with the decrease of the peak in repetitive cyclic voltammety observed with irreversible reactions involving soluble reactants and products caused by the decrease of the reactant concentration in the diffusion layer.¹⁰ We are thus dealing with another type of phenomenon, namely inhibition of the electrochemical process by the reaction product.¹¹ This is confirmed by the effect of increasing substrate concentration (Figure 1) and also by the effect of scan rate. The decrease of the peak upon repetitive cycling was indeed observed to become weaker and weaker upon raising the scan rate. This observation falls in line with the fact that the charge passed during a cycle and, thus, the amount of self-inhibiting product are decreasing functions of the scan rate. The effect of both scan rate and substrate concentration appears in the dimensionless parameter $p = (C^0/\Gamma^0)(RTD/Fv)^{1/2}$ (C^0 , substrate concentration, Γ^0 , maximal surface concentration of the inhibiting product, D , substrate diffusion coefficient, v , scan rate) which has been shown to govern self-inhibited cyclic voltammetric responses.^{11b}

With the exception of **9** and **10**, the same type of self-inhibition phenomenon is observed in the whole series of substrates. It however varies in intensity with the structure of the starting material. With **1–3** and **5–7**, the number of cycles required to completely passivate the electrode is of the same order and so is the effect of concentration. However, with **4** and **8**, self-inhibition is much slower. Fifty cycles are required to achieve total passivation instead of ca. 10 in the preceding cases. With **9** and **10**, the difference is even bigger since no self-inhibition could be observed.

The peak potentials observed with the various compounds during the first cycle at 0.1 V/s are listed in Table 1.

Reductive cyclic voltammety and X-ray photoelectron spectroscopy (XPS) are particularly suited for characterizing the

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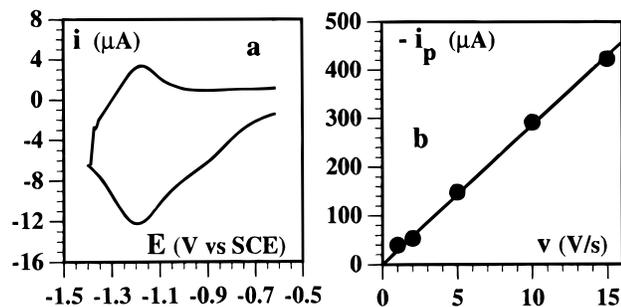
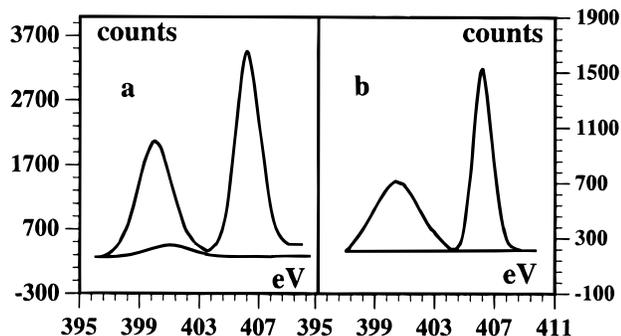
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Table 1. First-Cycle Peak Potentials

compd	1	2	3	4	5	6	7	8	9	10
E_p^a	0.98 ₆	0.93 ₅	0.82 ₅	0.30 ₈	0.78 ₀	1.16 ₃	0.88 ₅	0.41 ₀	0.91 ₈	0.73 ₀

^a At 0.1 V/s, in V vs SCE.**Table 2.** Chemical Composition, Derived from XPS, of Carbon Surfaces Derivatized by Oxidation of **6**^a

electrode material	% C total, 285–289 eV	% O total, 533 eV	% NO ₂ total, 406 eV	% reduced N, 400 eV	% CO ₂ H, 289 eV
GC	75.1 (90.0)	21.1 (9.5)	2.2 (0.0)	1.6 (0.4)	0.0 (0.0)
carbon fiber	70.8 (90.8)	27.7 (8.6)	2.3 (0.0)	0.0 (0.0)	0.0 (0.0)
HOPG	89.3 (99.7)	7.8 (0.3)	1.5 (0.0)	1.4 (0.0)	0.0 (0.0)

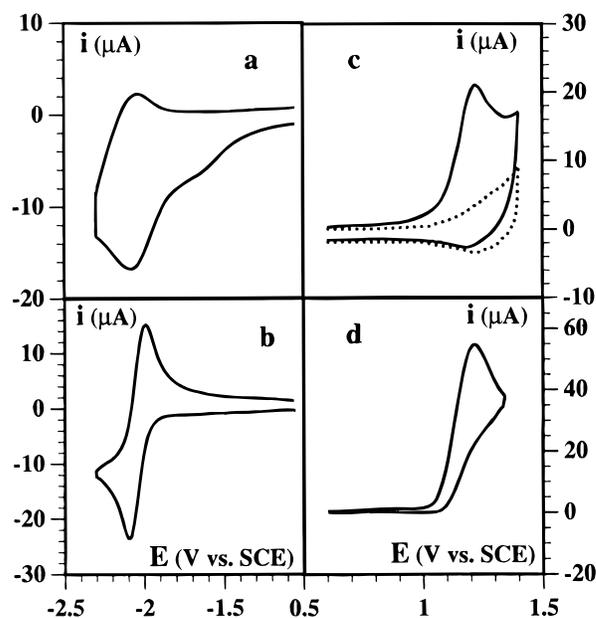
^a The composition of the fresh surfaces is given in parentheses.**Figure 2.** (a) Reductive cyclic voltammetry of a GC electrode passivated by oxidation of **6** and transferred to a pure electrolyte solution (acetonitrile + 0.1 M *n*-Bu₄NPF₆). Scan rate: 0.2 V/s. (b) Reductive cyclic voltammetry of solution of 0.35 mM nitrobenzene in the same electrolyte at a fresh GC electrode. Scan rate: 0.2 V/s. (c) Variation of the surface wave peak current with the scan rate.**Figure 3.** XPS spectra of carbon electrodes passivated by oxidation of **6** and transferred to a pure electrolyte solution (acetonitrile + 0.1 M *n*-Bu₄NPF₆): (a) GC, (b) HOPG. The base lines are the spectra of a fresh electrode in the same medium.

electrode coating in the case of **6** thanks to the presence of the *p*-nitro group. Figure 2a shows the cyclic voltammetric response of an electrode passivated by oxidation of **6** and transferred to a pure electrolyte solution. A reversible surface wave is observed in the same potential region as the solution wave of nitrobenzene ($E^0 = -1.1$ V vs SCE). The peak height is proportional to the scan rate (Figure 2b) as expected for a surface wave.¹² The large thickness of the surface wave falls in line with the existence significant repulsive interactions¹² between the nitrophenyl anion radicals formed upon reduction.

The presence of the 4-nitrobenzyl groups on the electrode surface is confirmed by XPS as shown in Figure 3 for a GC and a HOPG-electrode. The most prominent signal in both cases is that of the nitrogen of the nitro group at 406 eV.¹³ The

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**Figure 4.** (a) Reductive cyclic voltammetry of a GC electrode passivated by oxidation of **8** and transferred to a pure electrolyte solution (acetonitrile + 0.1 M *n*-Bu₄NPF₆). (b) Reductive cyclic voltammetry of a 0.61 mM solution of 9-methylanthracene in the same electrolyte at a fresh GC electrode. (c) Oxidative cyclic voltammetry of a GC electrode passivated by oxidation of **8** and transferred to a pure electrolyte solution (acetonitrile + 0.1 M *n*-Bu₄NPF₆). Dotted line: second scan. (d) Oxidative cyclic voltammetry of a 0.61 mM solution of 9-methylanthracene in the same electrolyte at a fresh GC electrode. Scan rate: 0.2 V/s.

smaller and less reproducible signal around 400 eV derives most probably from the nitrogen of reduced forms of the nitro group. The small pre-wave in the cyclic voltammetry of the grafted electrode (Figure 2), which is also not quite reproducible, has presumably the same origin. Similar observations were made with carbon electrodes grafted with 4-nitrophenyl radicals resulting from the reduction of the corresponding diazonium cation.⁵ The characteristics of the complete spectra on GC, HOPG, and also carbon fibers are summarized in Table 2. It is interesting to note that the 1s carbon signal of the carboxyl group at 289 eV is absent from the various spectra, in line with a reaction where CO₂ is expelled upon oxidation from the starting carboxylate prior grafting of the surface by the R groups.

Electrodes passivated by oxidation of **8** exhibit a similar behavior in reductive cyclic voltammetry (Figure 4). The presence of 9-methylanthryl groups on the surface is attested by the reversible surface wave (Figure 4a) located in the same potential region as the reversible solution wave of 9-methylanthracene (Figure 4b) in the same solution.

The presence of the (9-methylanthryl)methyl groups on the surface can also be detected by oxidative cyclic voltammetry.

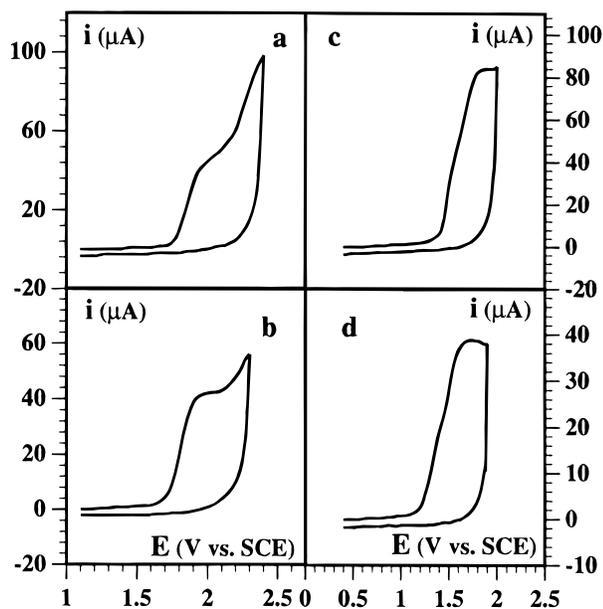


Figure 5. Oxidative cyclic voltammetry of a GC electrode passivated by oxidation of **1** (a), **2** (b), **3** (c), and **5** (d) and transferred to a pure electrolyte solution (acetonitrile + 0.1 M *n*-Bu₄NPF₆). Scan rate: 0.2 V/s.

A slightly reversible surface wave is indeed observed upon oxidative cycling of an electrode passivated by oxidation of **8** and transferred into a pure electrolyte solution (Figure 4c). This wave is located in the same potential range as the solution oxidation wave (Figure 4d).

GC electrodes derivatized by oxidation of **7** behave in a very similar manner (see Figure S1 in the Supporting Information) except that the oxidative cyclic voltammograms do not show any trace of reversibility. The reductive cyclic voltammogram at 0.2 V/s is less reversible than in the case of **8**, but reversibility can be restored upon raising the scan rate up to 20 V/s.

Electrodes passivated by oxidation of **1–3** and **5** are not expected to give a signal in reductive cyclic voltammetry since the corresponding hydrocarbons are not reduced before the discharge of the supporting electrolyte. The presence of the corresponding groups on the surface is however attested in oxidative cyclic voltammetry by irreversible waves (Figure 5) located in the same potential range as the solution irreversible peak of the corresponding hydrocarbons at the same scan rate (2.17, 1.98, 1.76, and 1.45 V vs SCE for toluene, *p*-xylene, anisole,¹⁴ and 1,2,3-trimethoxybenzene,¹⁴ respectively).

Derivatization by oxidation of **4** is an interesting case. Oxidative cyclic voltammetry of the passivated electrode in a pure electrolyte solution (Figure 6a,b) shows an oxidation wave in the same potential range as the solution oxidation wave of *N,N'*-dimethylaniline in the same medium. At a low scan rate (0.2 V/s), the wave is irreversible (Figure 6a,c). It becomes reversible (Figure 6b,d) upon raising the scan rate (20 V/s). The oxidation wave of *N,N'*-dimethylaniline is also irreversible at a low scan rate. However, two reduction waves appear upon scan reversal which correspond to the dimer dication formed during the anodic scan,¹⁵ whereas these two waves are absent in the reverse trace of the low scan rate voltammogram of the passivated electrode. Reversibility of the oxidation of *N,N'*-dimethylaniline in solution (Figure 6d) requires much higher scan rates to be reached¹⁵ than with the passivated electrode.

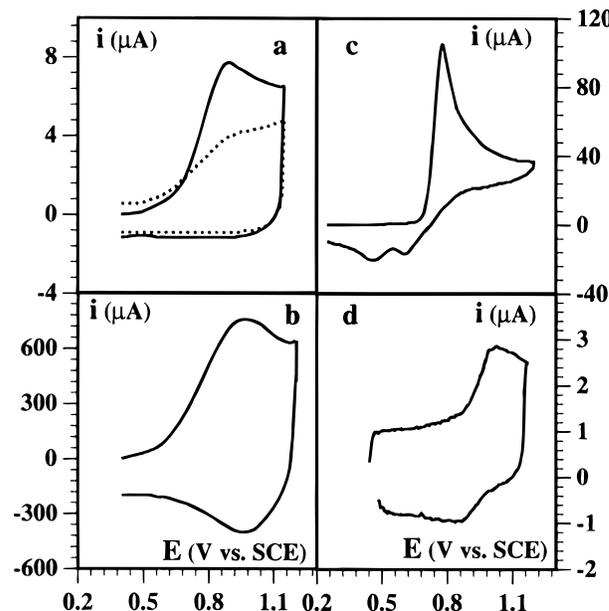


Figure 6. (a,b) oxidative cyclic voltammetry of a GC electrode passivated by oxidation of **4** and transferred to a pure electrolyte solution (acetonitrile + 0.1 M *n*-Bu₄NPF₆). Scan rate: 0.2 (a), 20 (b) V/s. Dotted line: second scan. (c,d) Oxidative cyclic voltammetry of a 2 mM solution of *N,N'*-dimethylaniline in the same medium. Scan rate: 0.2 V/s on GC (c) and 30 000 V/s on a 10- μ m-diameter Pt ultramicroelectrode (d).

Table 3. Characteristic Distances (\AA) between the Anchoring Points in HOPG Surfaces Grafted with 1-Naphthylmethyl and 9-(10-Methylantrhylyl)methyl Groups

	7		8	
	STM	model	STM	model
shortest side	14.5	14.6	15.1	14.9
longest side	19.5	18.6	22.3	21.2
shortest diagonal	25.2	23.0	24.3	23.7

These observations show that the chemical reactions following electron transfer are different, in line with the fact that the 4-*N,N'*-dimethylbenzyl moieties are attached to the surface rather than dispersed in the solution.

Scanning electron tunneling microscopy¹⁶ offers an additional means to characterize the passivated surfaces. Figure 7 shows the STM images obtained on clean HOPG and after passivation of the surface by oxidation of **7** and **8**. Cyclic voltammetry after oxidation, in the conditions described in the caption of Figure 7, revealed that the electrode was completely passivated, thus showing that the maximum coverage was reached. After passivation, the HOPG surface was carefully rinsed with three solvents, acetone, ethanol, dichloromethane. Ultrasonication was however avoided since it destroys the HOPG surface. With both **7** and **8**, the electrochemical treatment results in a drastic change of the image. A regular array of large white spots appears. The dimension of each spot, ca. 1.3 nm, is consistent with the area covered by the 1-naphthylmethyl or 9-(10-methylantrhylyl)methyl groups freely rotating around the arylmethyl carbon. The analysis of the STM images, after Fourier transformation, suggests the distribution of the surface anchoring carbons depicted in the bottom diagrams of Figure 7. The sizes of the parallelograms in the model and in the experimental STM images (upper diagrams of Figure 7) are compared in Table 3.

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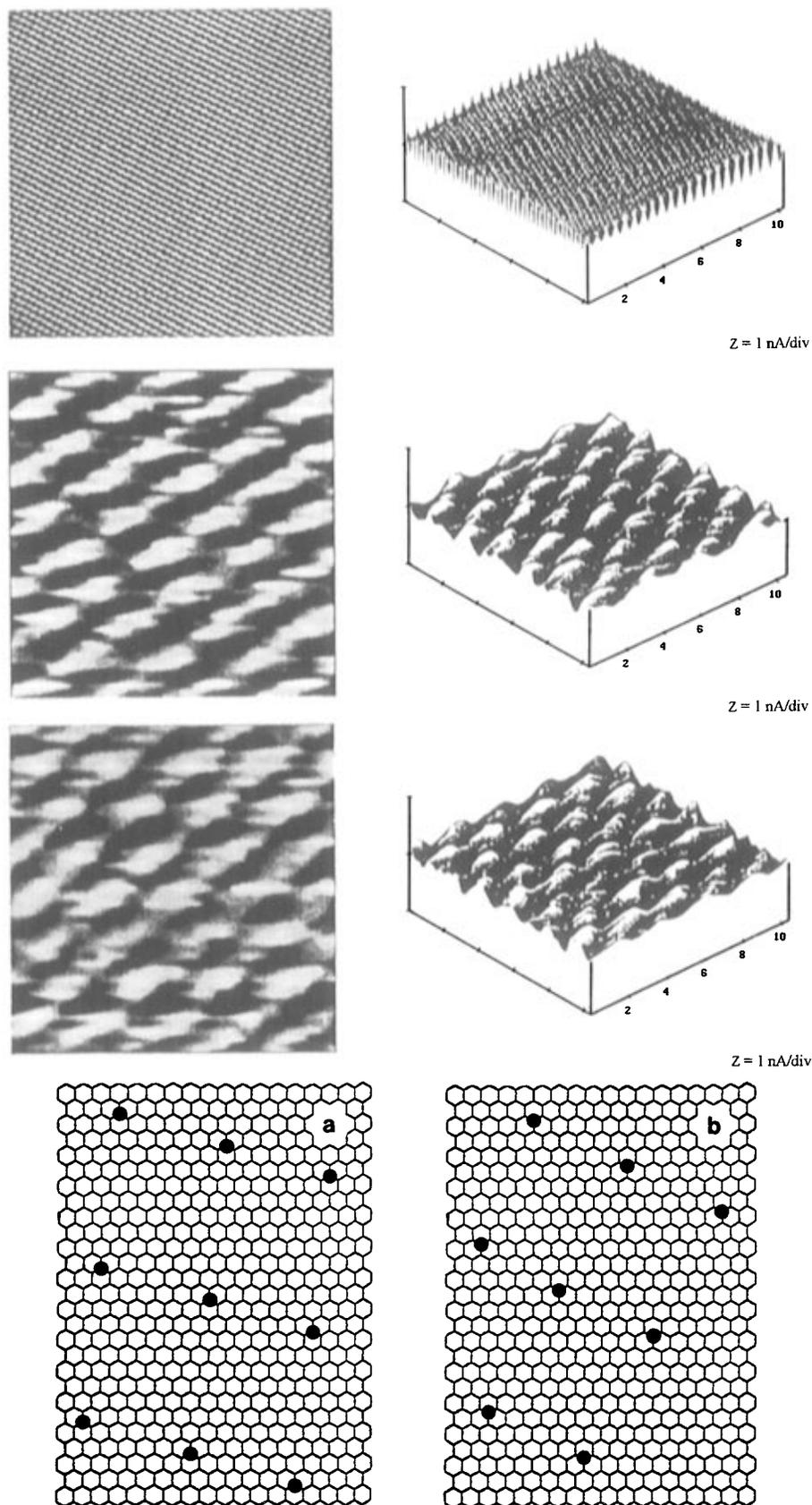


Figure 7. (top) Bi- and tridimensional 10×10 nm STM images of HOPG surfaces. From top to bottom: clean surface, surface derivatized by oxidation of **7** (at a potential of 1.10 V vs SCE during 15 min in a 2 mM solution), surface derivatized by oxidation of **8** (at a potential of 0.65 V vs SCE during 30 min in a 1 mM solution). Bias potential: 17, 43, and 37 mV, respectively. (bottom) Model distribution of the anchoring arylmethyl carbons after passivation of the HOPG surface by **7** (a) and **8** (b).

Using Dreiding models, it is seen that the distance between two anchoring points in the arrangement shown in Figure 7 is slightly larger than twice the rotation radius of the grafted group.

We may thus conclude that the HOPG surface is covered by a monolayer of freely rotating 1-naphthylmethyl and 9-(10-methylanthryl)methyl groups in the cases of **7** and **8**, respectively

(the number of moles per square centimeter on the surface is 0.50×10^{-10} and 0.53×10^{-10} , respectively).

The coverage of the GC surfaces grafted by oxidation of the carboxylates may be approximately estimated when the attached group gives rise to a reversible reduction wave as in the cases of **6**–**8**. The charge corresponding to the one-electron reduction of the attached groups is obtained by integration of the cyclic voltammograms of the grafted electrodes (Figures 2a, S1a, and 4a, respectively). Because of the roughness of the surface, the actual surface area is larger than the geometrical surface area. Measuring the amount of methylene blue adsorbed on our GC electrodes and comparing it with the amount adsorbed on a mercury surface¹⁷ of known surface area showed that the ratio between the actual is larger and the geometrical surface areas is approximately three. It follows that the surface concentrations of the grafted groups are 2.5×10^{-10} , 1.5×10^{-10} , and 1.4×10^{-10} mol cm⁻² for **6**, **7**, and **8**, respectively. It thus appears, although these later determinations are certainly quite approximate, that the surface concentrations are larger on GC surfaces than on HOPG surfaces, pointing to the conclusion that edge carbon atoms are more reactive than basal plane carbons toward grafting.

The fact that, with GC electrodes, the surface can only be cleaned up by abrasion points to a covalent attachment of the alkyl groups. What is the mechanism of the reaction that leads to the grafting of the electrode by the arylmethyl group? The arylmethyl radical produced by reaction 1 is in all cases easier to oxidize than the starting molecule.¹⁸ It should thus be oxidized into the corresponding carbocation at the potential where it is generated. For the next step, one may envision a reaction of this carbocation with one of the surface carbon atoms, thus leading to a surface bearing one positive charge on a neighboring carbon. This will however be immediately neutralized by one electron coming from the bulk of the electrode since the surface electron density is governed by the electrode potential and the composition of the bathing electrolyte. Thus, overall, the grafting reaction amounts to the reaction of one arylmethyl radical with the surface. In the case where basal planes are exposed to the solution, an unpaired electron should thus appear on a neighboring carbon which will be paired off after the grafting of a second radical and so forth during the reaction of further radicals with the surface. Competitively, the arylmethyl cation may diffuse away from the surface and react with the solvent or other nucleophiles present in the solution.

Within this framework, the observation that oxidation of **9** and **10** does not give rise to any grafting of the graphite surface by the corresponding arylmethyl groups falls in line with the intuitive notion that diphenyl and triphenylmethyl radicals are less reactive than the benzyl and substituted benzyl radicals.

Electrochemical Erasing of the Grafted Films. As seen in Figures 4–6 and S1 (Supporting Information), the oxidation waves of the grafted groups are irreversible at low scan rates. These waves disappear or almost disappear after a second anodic scanning of the electrode potential (as represented by a dotted line in Figures 4, 6, and S1 for **8**, **4**, and **7**, respectively). In all cases, holding the potential of the grafted electrode in a pure electrolyte solution for a few minutes slightly beyond the oxidation peak and then retransferring the electrode into the carboxylate solution that served to prepare it leads to the restoration of its initial properties. The electrode thus treated exhibits the same behavior toward passivation by carboxylate oxidation as a clean electrode (Figure 1).

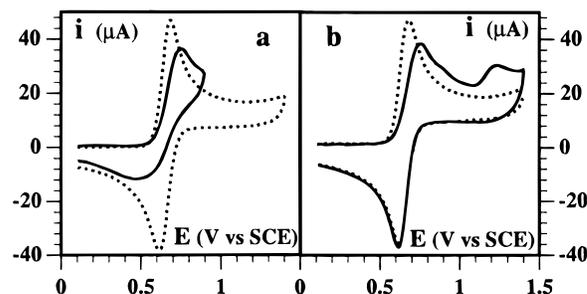


Figure 8. Cyclic voltammetry of ferrocene carboxylic acid (1.2 mM) on a GC electrode in acetonitrile + 0.1 M *n*-Bu₄NPF₆ at 0.2 V/s: (a) clean electrode (dotted line), electrode passivated by oxidation of **8** stopping the scan before the film wave (solid line); (b) electrode passivated by oxidation of **8** scanning beyond the film wave, first scan (solid line), second scan (dotted line).

Another way of observing the same phenomenon is to look at the cyclic voltammetric response of a reversible couple at a grafted before and after electrochemical erasing of the film. One such experiment is represented in Figure 8. On a clean GC electrode, ferrocene carboxylic acid gives rise to a reversible wave (Figure 8a). On a GC electrode grafted with 9-(10-methylanthryl)methyl groups obtained by anodic oxidation of **8**, a less reversible wave is observed (Figure 8a) when the scan is reversed before the oxidation wave of the 9-(10-methylanthryl)methyl groups in the film. This apparent slowing of the electron transfer is what is expected for an electrode covered by an insulating film containing numerous and small holes through which the electron transfer can occur as a result of the interference in the mass transport process of constrained diffusion toward and from the holes.¹⁹ If scan reversal is located beyond the oxidation wave of the 9-(10-methylanthryl)methyl groups, the first-scan cathodic wave exhibits the same behavior as the cathodic wave at a clean electrode (Figure 8b). During the second scan, both the anodic and cathodic waves of ferrocene carboxylic acid are the same as those obtained at a clean electrode. These observations confirm that the deposited film is removed by slow-scan oxidation of the 9-(10-methylanthryl)-methyl groups it contains.

Second Grafting Process. Anodic oxidation of the arylmethyl carboxylate ions by means of a potential scanning just encompassing the oxidation wave leads to the grafting of the corresponding arylmethyl groups onto the carbon surface. As a result, the oxidation wave gradually disappears, indicating that the electrode becomes passivated toward further oxidation of the arylmethyl carboxylate ions. However, once this first grafting process has been completed, the cyclic voltammetry of the electrode thus modified in the same carboxylate solution shows the presence of a more positive oxidation wave located between the initial carboxylate oxidation wave and the oxidation wave of the arylmethyl groups which was observed when the grafted electrode was transferred into a pure electrolyte solution (Figure 9).

Cycling the potential up to the peak of this new wave leads to progressive passivation in the same way as already observed for the initial oxidation wave. Cyclic voltammetry after ultrasonication and transfer of the electrode thus passivated into a pure electrolyte solution again shows the characteristic surface waves of the grafted arylmethyl groups. These are shown in Figure 10 for the reduction of the 1-naphthylmethyl or 9-(10-methylanthryl)methyl groups grafted upon oxidation of **7** and **8**. We also note that the amount of

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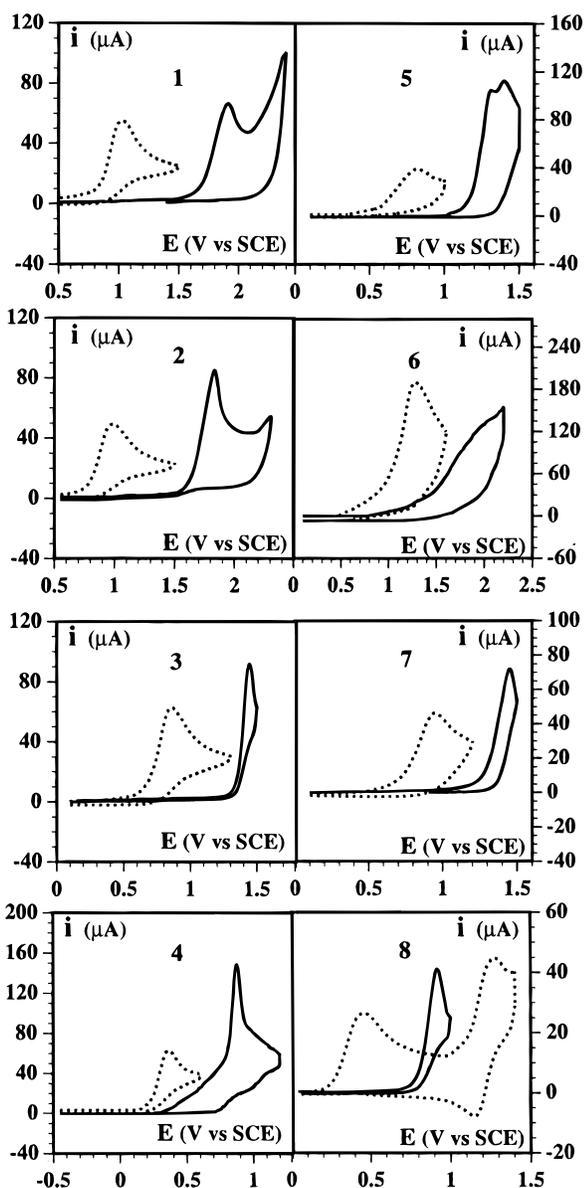


Figure 9. Cyclic voltammetry of the arylmethyl carboxylates 1–5 (2 mM), 6 (5 mM), 7 (2 mM), and 8 (1 mM) at a GC electrode in acetonitrile + 0.1 M *n*-Bu₄NPF₆ at 0.2 V/s. Dotted lines: initial oxidation of the carboxylate. Solid lines: oxidation of the carboxylate after passivation at the initial oxidation wave.

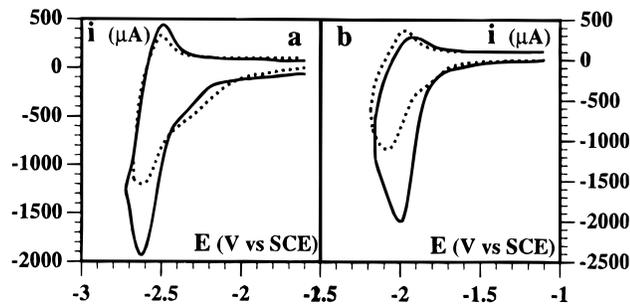


Figure 10. Cyclic voltammetry at 20 V/s of GC electrodes derivatized by oxidation of 7 and 8 at the initial oxidation wave (dotted lines) and by the second grafting process (solid lines) after transfer in a pure acetonitrile + 0.1 M *n*-Bu₄NPF₆ solution.

aryl methyl groups attached to the surface is larger in the second grafting process than in the first (Figure 10).

The latter conclusion is confirmed by the comparison between STM images obtained on HOPG after each of the grafting

Table 4. Characteristic Distances (Å) between the Anchoring Points in HOPG Surfaces after the Second Derivatization by 1-Naphthylmethyl and 9-(10-Methylantrhyl)methyl Groups

	7		8	
	STM	model	STM	model
shortest side	8.2	8.4	8.0	8.4
longest side	11.0	11.1	11.1	10.5
shortest diagonal	12.2	12.6	11.2	10.4

processes (Figure 11). Comparing the STM images and the ensuing arrangement of the anchoring points (Figure 11 vs Figure 7) shows that the characteristic distances are shorter in the first case than in the second (Table 4 vs Table 3). The surface coverage is about 5 times larger after the second grafting process than after the first. Another way to confirm the presence of a denser film on the carbon surface is to observe the oxidation or the reduction of compounds in solution that give rise to reversible responses at a bare electrode. This is what is shown in Figure 12 for the oxidation of ferrocene and the reduction of benzoquinone. The first derivatization by oxidation of 1 at its initial wave leads to a decrease of the apparent electron transfer rate constant as already observed with ferrocene carboxylate (Figure 8). The second derivatization leads to strong passivation of the electrode surface, thus showing that the surface is covered with a more compact film.

The compact film deposited during the second derivatization process can also be erased after transfer of the electrode to a pure electrolyte solution by setting the electrode potential beyond the oxidation wave of the grafted groups as for the film obtained by the first derivatization process.

These observations may be explained as follows. During the first derivatization process, passivation of the electrode toward further oxidation of the arylmethyl carboxylate ions results from the deposition of an insulating layer of arylmethyl groups. However the surface contains microscopic sites where electron transfer can still take place. Indeed, when the same electrode is transferred, after ultrasonic rinsing, to a pure electrolyte solution, solutes can still be oxidized or reduced, albeit with a decreased electron transfer rate constant. Thus, the complete passivation of such an electrode toward further oxidation of the arylmethyl carboxylate ions results not only from the presence of the insulating arylmethyl groups but also from the blocking of the remaining uncovered sites by the carboxylate ions. It is indeed conceivable that the neighboring arylmethyl groups can induce a significant decrease of the local dielectric constant, thus causing a strong electrostatic attraction between the carboxylate ions and the positively charged electrode surface. The oxidation of the carboxylate ions thus adsorbed requires a higher energy than the oxidation of free carboxylate ions at a bare surface. These are the reasons that total passivation of the surface at the potential of the first oxidation wave is observed in a solution containing the carboxylate and also that, at the electrode thus passivated and in the same solution, a second, more positive, oxidation wave is observed leading to further derivatization of the surface. This interpretation falls also in line with the observation that the second wave is sharper than the first, indicating that it involves the oxidation of an adsorbed species.

Conclusions

Electrochemical oxidation of carboxylates according to the Kolbe reaction offers a simple and efficient means to covalently graft arylmethyl groups on carbon surfaces. The starting molecules are easily accessible, and the presence of appropriate substituents on the phenyl rings makes this type of derivatization

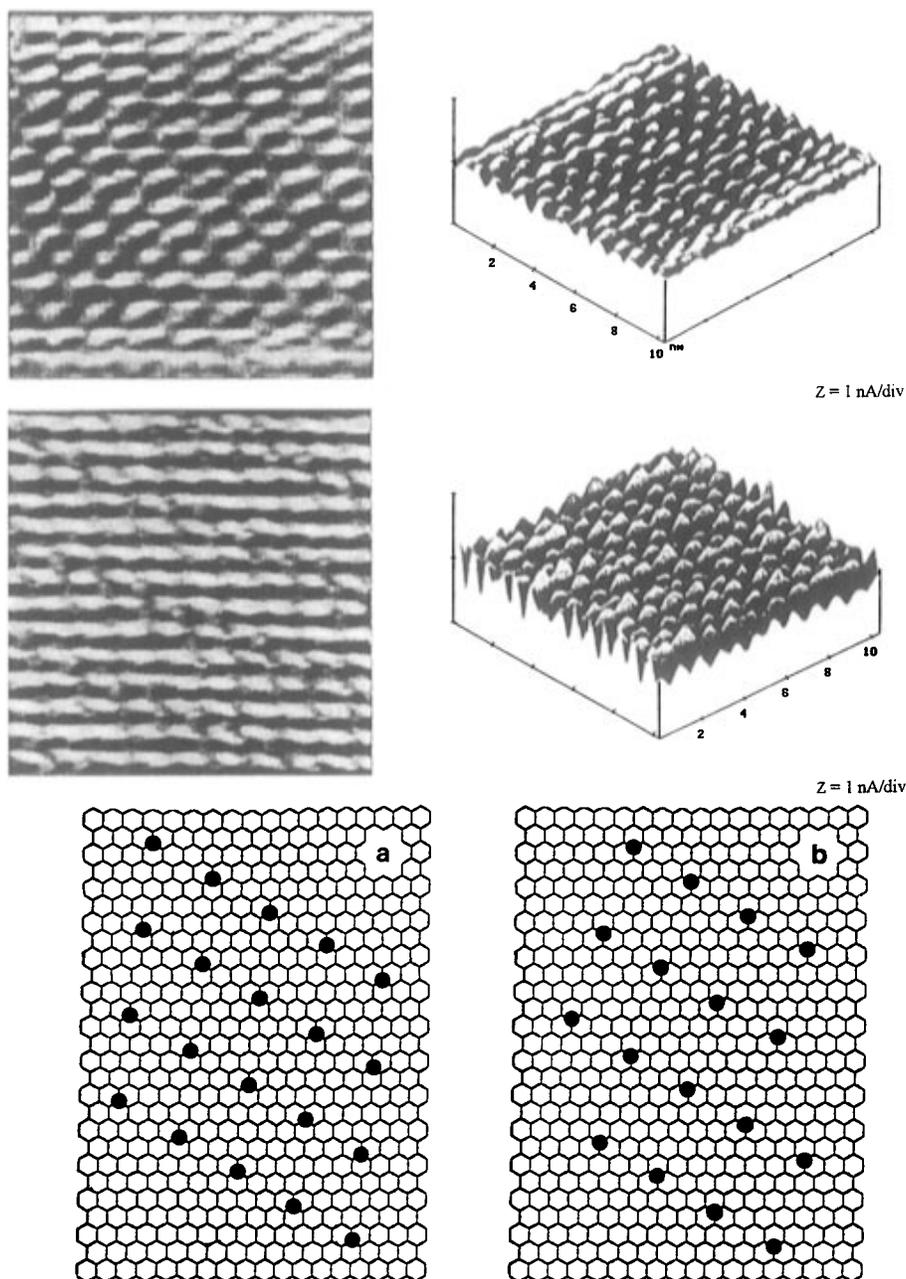


Figure 11. (top) Bi- and tridimensional 10×10 nm STM images of HOPG surfaces. From top to bottom: surface derivatized by oxidation of **7** (2 mM) at 1.1 V vs SCE during 15 min and then at 1.5 V vs SCE during 15 min, surface derivatized by oxidation of **8** (1 mM) at 0.65 V vs SCE during 30 min and then at 0.95 V vs SCE during 30 min. Bias potential: 1.2 mV. (bottom) Model distribution of the anchoring arylmethyl carbons after passivation of the HOPG surface by **7** (a) and **8** (b).

a convenient starting point for further chemical modifications. Cyclic voltammetry allows one to follow the extent of the surface modification as a function of the number of successive potential cycles. The presence of the groups on the surface is clearly attested by the same technique as well as by XPS after transfer of the derivatized electrode into a pure electrolyte solution. The STM images obtained with grafted HOPG electrodes reveal the arrangement of the anchoring points, and their analysis indicates that one monolayer of arylmethyl groups is attached on the surface. The same conclusion also results from the cyclic voltammetry of derivatized GC electrodes. The very fact that such cyclic voltammograms can be obtained demonstrates that the grafted groups are in electrical contact with the electrode by means of electron hopping to or from the aryl moieties they contain. Once the electrode has been derivatized in this manner, two types of electrochemical manipulation of the derivatized surface can be performed. One

is that the coatings can be made more compact by further grafting arylmethyl groups at the potential of a second, more positive oxidation wave, where the electrostatically adsorbed carboxylate ions become oxidized. The densification of the film is attested by the cyclic voltammetric responses and by the changes in the STM images obtained on HOPG. Another possible electrochemical manipulation consists of erasing the grafted arylmethyl groups after transfer to a pure electrolyte solution by setting the electrode potential at the level of their oxidation wave.

Experimental Section

Chemicals. The solvent, acetonitrile, was a Merck product (Uvasol grade). The supporting electrolyte, *n*-Bu₄NPF₆, was purchased from Fluka (puriss. > 99%). They were both used without further purification.

(9-Methyl-10-anthryl)acetic acid was prepared from 9-methylantracene by adaptation of the method previously described for the

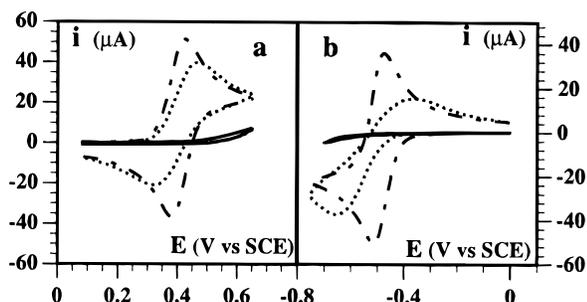


Figure 12. Cyclic voltammetry of 1.4 mM ferrocene (a) and 1.4 mM benzoquinone (b) in acetonitrile + 0.1 M *n*-Bu₄NPF₆ at 0.2 V/s on a clean GC electrode (dashed lines), after derivatization by benzyl groups on the first oxidation wave of **1** (dotted lines) and after the second derivatization (solid lines).

synthesis of 9-anthrylacetic acid.¹⁹ All other acids were Aldrich or Fluka products. The corresponding carboxylates were prepared in the electrochemical cell by addition of a stoichiometric amount of *n*-Bu₄NOH.

Cyclic Voltammetry. The working electrode was a 3-mm-diameter GC disk (Tokai). It was polished before each experiment using successively sandpaper and 15, 6, and 1 μm diamond pastes and rinsed with acetone and ethanol under ultrasonic agitation. The counter electrode was a platinum wire and the reference electrode an aqueous SCE.

The instrument consisted of a function generator (PAR, model 175 Universal Programmer) and a home-built potentiostat and current measurer equipped with positive feedback compensation.²⁰

XPS. The XPS spectra were recorded with an ESCALB MK1 spectrometer equipped with an aluminum anode delivering Al Kα

photons (1486.6 eV) working under 200 W. The sample was placed in a 10⁻⁸ mbar vacuum chamber.

The GC samples were 2 × 1 cm Tokai GC plates. There were carefully polished and rinsed between each experiment according to the same procedure as for the CV working electrodes. Derivatization was carried out by dipping the plate in a 1–5 mM solution of the carboxylate in acetonitrile (+0.1 M *n*-Bu₄NBF₄) and imposing during 10 min a potential slightly positive to the cyclic voltammetric peak potential by means of the same three-electrode configuration and instrument as for cyclic voltammetry. The HOPG samples were Tokai plates fixed on a metal disk with a silver glue. Clean surfaces were obtained by peeling off the top graphite layers. Derivatization was carried out by the same procedure as already described for GC plates. The surfaces thus obtained were carefully rinsed before transfer of a pure electrolyte solution in the same solvents as for GC but with no ultrasonic agitation.

STM. The STM images were obtained with a Digital Instrument Nanoscope III microscope in a constant-height mode with a current in the range 1–3 nA and a bias potential of 1–42 mV. The HOPG samples were prepared as in the XPS experiments.

Acknowledgment. We are grateful to Prof. J. Pinson and Dr. O. Fagebaume for helpful discussions on many aspects of the work. We thank Prof. M. Delamar for his precious assistance in using XPS and P. Guiriec for his help in STM experiments.

Supporting Information Available: Cyclic voltammogram for **7** (1 page). See any current masthead page for ordering or Internet access instructions.

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