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Covalent Modification of Iron Surfaces by Electrochemical Reduction of Aryldiazonium Salts

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Abstract: Electrochemical reduction of aryldiazonium salts (in acetonitrile or acidic aqueous medium) on an iron or mild steel surface permits the strong bonding (which resists an ultrasonic cleaning) of aryl groups on these surfaces. Attachment of aryl groups was demonstrated by the combined used of electrochemistry, infrared spectroscopy and polarization modulation infrared reflection spectroscopy (PMIRRAS), Rutherford backscattering, X-ray photoelectron spectroscopy, and capacity measurements. The substituents of aryl groups, which can be widely varied, include NO_2, I, COOH, and long alkyl chains. It is shown that the attachment of the aryl groups is to an iron and not to an oxygen atom and that the bond is covalent.

Introduction

We have shown previously that the electrochemical reduction of aryl diazonium salts on a carbon electrode permits the covalent attachment of the aryl groups to the carbon surface.[1] The above electrochemical reaction can be performed in ACN but also in acidic aqueous medium. The monolayers obtained with a variety of starting diazonium salts have been characterized by cyclic voltammetry, X-ray photoelectron spectroscopy (XPS), polarization modulation infrared spectroscopy (PMIRRAS), Raman spectroscopy,[2] and Rutherford back scattering (RBS). The grafting of aryl groups takes place on glassy carbon with surface pending bonds but also on the basal plane of highly oriented pyrolytic graphite (HOPG).[1,2] On the basis of the thoroughly investigated electrochemical reduction of aryl halides,[3] the grafting was assigned to the reaction of the very reactive aryl radical produced upon one-electron reduction of the diazonium cation.[1] The structure of the layer was examined by AFM[4a] and STM[4b] and it was concluded[4a] that the layer can be thicker than a monolayer. The electrochemical blocking properties of the films produced by this method have been investigated.[5] These organic monolayers have been used to attach redox enzymes,[1b,6] to reduce protein adsorption,[7a] to differentiate the electrochemical signals of dopamine and ascorbic acid,[7b] and to control the selectivity of glassy carbon flow detectors.[7c] The mere reaction of aryl diazonium salts (without electrochemistry) has permitted the attachment of aryl groups to carbon black to produce materials which may be useful in the plastic, rubber, and textile industries.[8] It is also possible to obtain closed packed aryl layers on silicon[9] by electrochemical reduction of diazonium salts on H-terminated Si (111).

It was therefore interesting to find out whether this process could be extended to other substrates; in this paper we shall describe the modification of iron and mild steel surfaces.[10] Besides adhesion and lubrication, the modification of biomedical surfaces, an obvious application of such a process would be the protection of iron and steel against corrosion and we shall

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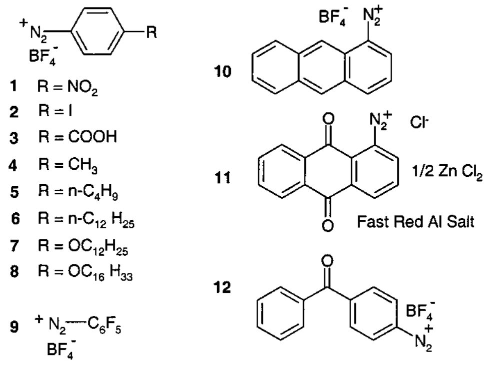
Scheme 1



discuss this point in a forthcoming paper. The experiments have been performed both on chemically pure iron and mild (the practical material which should be protected against corrosion) and stainless steel. In the same way both acetonitrile and acidic aqueous solutions have been utilized, the use of the first solvent is, as we shall see later, much more convenient but of little practical relevance. The different diazonium salts which have been investigated are shown in Scheme 1. Compounds **1**, **3**, **11**, and **12** were investigated as their substituents are easily characterized by cyclic voltammetry (NO_2, quinone, benzoylphenyl), XPS or RBS (NO_2, I, COOH), and IR (NO_2, benzoylphenyl); the other diazoniums were selected because they could provide an alternative to thiols on gold but also for their possible hydrophobic properties from which one could expect some anticorrosion efficiency.

Results

Electrochemical Evidence for the Surface Modification. The possibility of grafting aryl groups on iron surfaces has been investigated in both aprotic [acetonitrile (ACN) + 0.1 M NBu_4BF_4] and acidic aqueous (diazonium salts are not stable in aqueous solution above pH 2) media. In ACN + 0.1 M NBu_4BF_4 an iron electrode presents an electroactivity domain that is restricted from −0.1 to −2.3 V/SCE (Figure 1a). In dilute (0.1 N) sulfuric acid this domain shrinks to nothing (Figure 1b). The open circuit potential (corrosion potential)[11,12] is located at −0.58 V/SCE, corresponds to a mixed potential since the oxidation and reduction reactions are different, and is reached when the anodic and cathodic currents are equal. The electroactivity domains are therefore completely different from that of a carbon electrode and it is not possible to observe as described earlier[1] the reduction wave of diazonium salts which are located at potentials positive to the oxidation of the metal. If the diazonium is substituted by an electron donating group as in the case of **5**, the reduction potential becomes negative enough to permit the observation of the reduction wave by cyclic voltammetry (Figure 2a). However, in the case of **1** bearing a nitro electron withdrawing group, the wave becomes too positive to be observed before the oxidation of iron. Therefore, in ACN, the only general way to achieve the grafting of aryl groups on the iron surface is to set the potential more negative than the reduction of the diazonium salt, whether or not the cyclic voltammetry wave can be observed. Coming back to the voltammogram of **5**, one observes the decrease of the wave on the second scan (Figure 2b) and its total disappearance after 30 s of electrolysis (Figure 2c); this is similar to what has been previously observed on carbon. In sulfuric acid one should set the potential negative to the corrosion potential (we will see

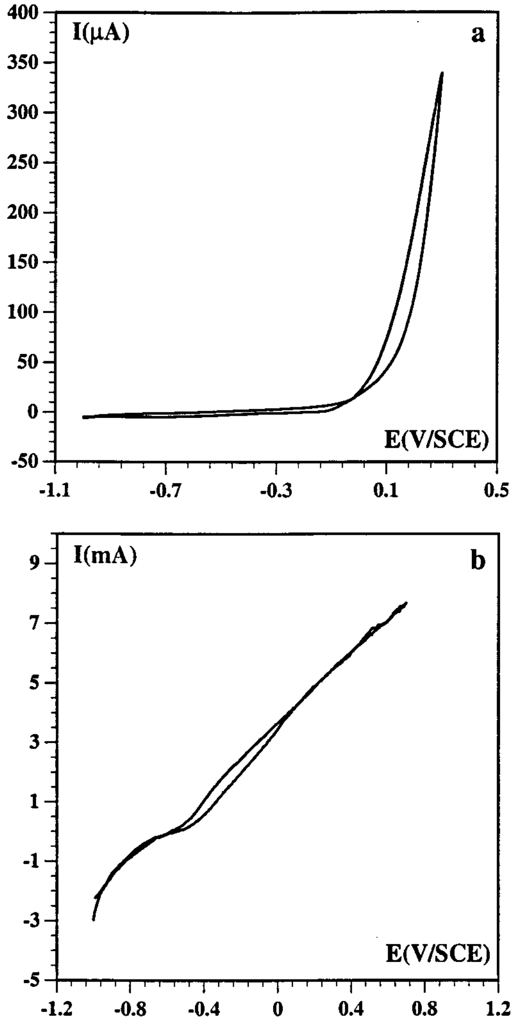


Figure 1. Cyclic voltammogram on a 1 mm diameter iron electrode in (a) ACN + 0.1 M NBu_4BF_4, scan rate $v = 0.2$ V/s, and (b) 0.1 N H_2SO_4, scan rate $v = 0.02$ V/s, with SCE reference.

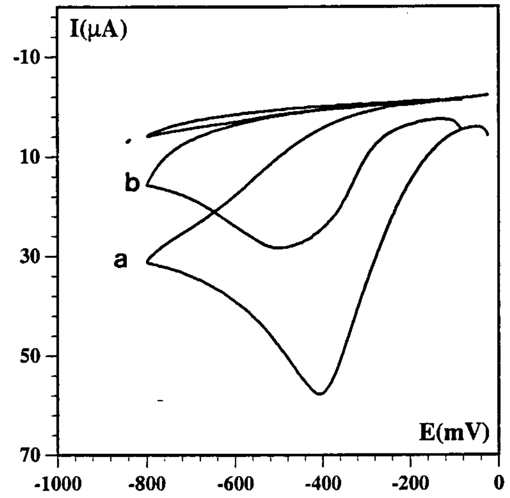


Figure 2. Cyclic voltammetry of **5** ($c = 2$ mM) in ACN + 0.1 M NBu_4BF_4, 1 mm diameter iron electrode, scan rate $v = 0.2$ V/s, SCF reference: (a) first cycle, (b) second cycle, and (c) after 30 s of electrolysis.

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later that it is possible to determine an optimal potential for this grafting reaction at −0.75 V/SCE in 0.1 N H_2SO_4). With such a procedure one assumes that diazonium salts are reduced at similar potentials on carbon and iron. The reduction potential of diazonium salts and the oxidation potential of iron in aqueous media should make the direct reduction of diazonium salts by iron thermodynamically possible. However, we shall see later through XPS measurements that this spontaneous reaction is unimportant for the grafting of the surface.

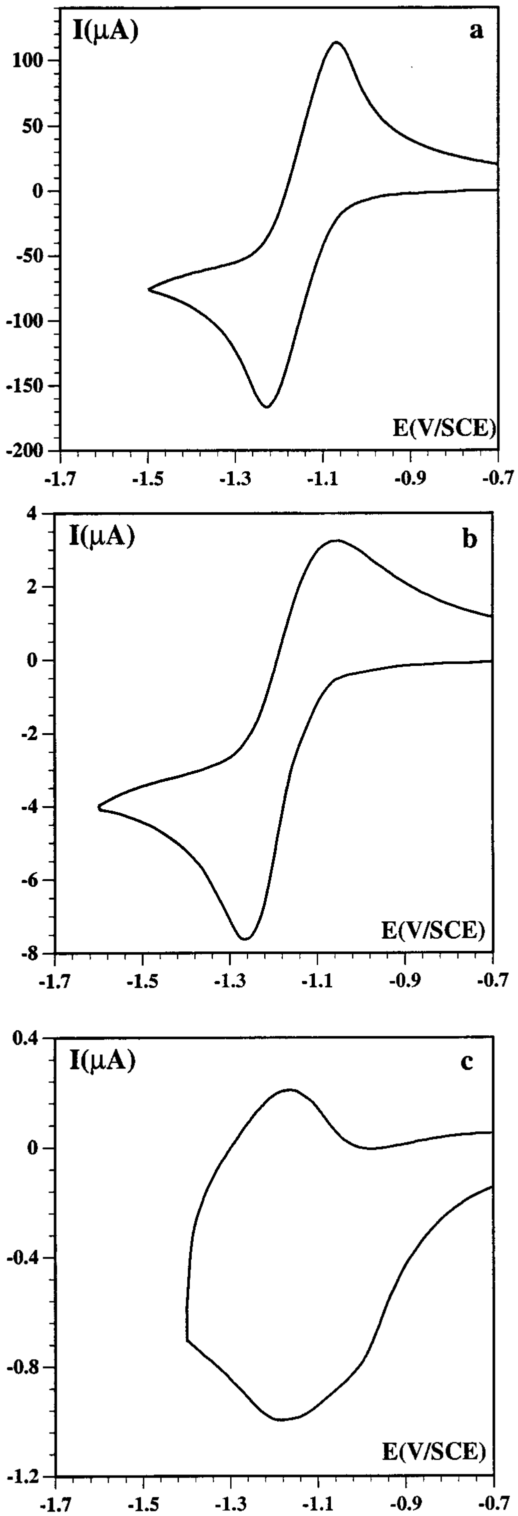

Figure 3. Cyclic voltammetry in ACN + 0.1 M NBu_4BF_4 of nitrobenzene ($c = 2$ mM) on (a) a glassy carbon electrode and (b) on an iron electrode and (c) of an iron electrode derivatized with 4-nitrophenyl groups (see text), with $v = 0.2$ V/s and SCE reference.

We have investigated the reduction of 4-nitrobenzenediazonium tetrafluoroborate **1**, which on carbon leads to the attachment of 4-nitrophenyl groups. These groups are easily characterized by their reversible reduction wave in aprotic medium located at the same potential as nitrobenzene itself. We first recorded the cyclic voltammogram of nitrobenzene in ACN + 0.1 M NBu_4BF_4 on an iron electrode; one observes two waves at −1.22 and −1.75 V/SCE (not shown), the height of the second one being about double that of the first. The first wave is reversible as an anodic wave is observed at −1.00 V/SCE on the return scan. The standard potential of nitrobenzene is therefore $E° = -1.11$ V/SCE. This voltammogram is similar to that observed on carbon electrodes (Figure 3). Then, the potential of an iron electrode was maintained during 5 min at −0.8 V/SCE in an ACN + 0.1 M NBu_4BF_4 solution containing **1** ($c = 2$mM). Thereafter the electrode was carefully rinsed in acetone in an ultrasonic bath for 5 min in the absence of oxygen and transferred to a new solution containing only the solvent and the supporting electrolyte. Under such conditions, one can observe a very broad reversible wave ($E_{pc} = -1.17$ V/SCE and $E_{pa} = -1.16$ V/SCE) at a potential very close to that of nitrobenzene itself (Figure 3c). This experiment clearly indicates that nitrophenyl groups are transferred with the electrode and that their bonding is strong enough to resist rinsing in an ultrasonic bath. Figure 4 presents the result obtained with Fast Red Al salt **11**, which is a commercial diazonium salt of anthraquinone. The iron electrode, which had been derivatized and carefully rinsed under the same conditions as above, presents a reversible system with a cathodic peak at $E_{pc} = -0.93$ V/SCE and an anodic peak at $E_{pa} = -0.88$ V/SCE, which corresponds to a standard potential $E° = -0.90$ V/SCE. By comparison, anthraquinone exhibits on an iron electrode a slow redox wave ($E_{pc} = -1.08$ V/SCE and $E_{pa} = -0.75$ V/SCE) with $E° = -0.91$ V/SCE, i.e., at the same potential as the modified electrode. This experiment confirms the observations made with **1**. In addition, the symmetrical shape of the voltammogram is indicative of a system that does not diffuse to and from the electrode as could be expected for molecules bonded to the electrode. It was also possible to observe the remarkable stability of the system on repetitive scanning. Similar results were also obtained with anthracenyl groups bonded to the surface through reduction of **10** (Figure S1 in the Supporting Information).

An iron electrode modified by reduction of **11** at $E = -0.5$ V/SCE in 0.1 N H_2SO_4 carefully rinsed and transferred to an ACN + 0.1 M NBu_4BF_4 solution presents a voltammogram with a low reversibility ($E_{pc} = -0.9$ V/SCE and $E_{pa} \approx -0.6$ V /SCE) at $E° \approx -0.7$ V/SCE. This voltammogram (Figure 5) is very similar to that of anthraquinone in ACN + 0.1 M NBu_4BF_4 on an iron electrode previously maintained in a 0.1 N H_2SO_4 solution for 5 min. These experiments in acidic aqueous solution indicate that it is possible to obtain the attachment of aryl groups to the iron surface but the voltammogram of these aryl groups is modified by reference to that obtained after grafting in ACN. This appears through a loss of reversibility and a slower electronic transfer. The loss of reversibility can be related to the protonation of the radical anions by acidic species transferred with the electrode despite vigorous rinsing.

The modification of the iron surface is therefore possible in ACN and acidic aqueous solution, but is more easily observed after grafting in ACN. These results called for a characterization of the surface by independent methods.

Infrared Spectra of the Organic Layer. As in the case of monolayers on carbon it is difficult to obtain significant

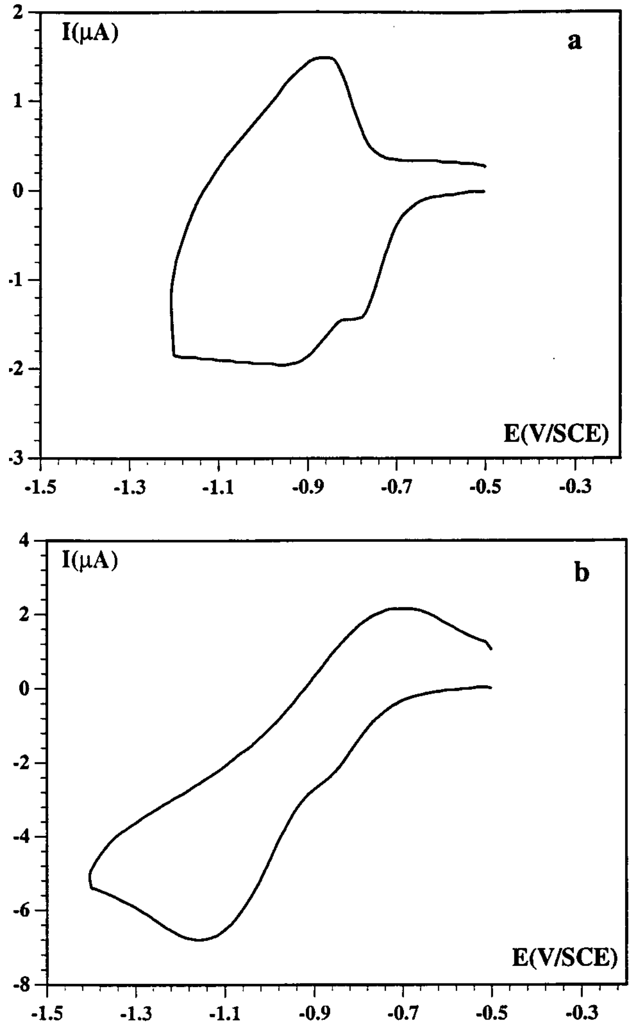

Figure 4. Cyclic voltammetry of (a) an iron electrode modified with anthraquinone groups and transferred to an ACN + 0.1 M NBu_4BF_4 solution and (b) an iron electrode in an ACN + 0.1 M NBu_4BF_4 + 3mM anthraquinone solution, with $v = 0.2$ V/s and SCE reference.

reflection infrared spectra of monolayers. However, this can be achieved with polarization modulation infrared absorption spectroscopy.[13] The spectra were obtained with mild steel plates for which a protection against corrosion would be of interest. Before grafting, the steel plates were carefully polished and rinsed in the absence of oxygen in an ultrasonic cleaner. An ungrafted plate presents absorptions at 1050−1100 cm^{-1} characteristic of oxides as well as absorptions at 1400 and 1600−1700 cm^{-1} related to carbonates and hydrogenocarbonates (most likely stemming from reaction with atmospheric carbon dioxide after grafting) (Figure 6a). After grafting by **1** in an ACN + 0.1 M NBu_4BF_4 solution the symmetrical and antisymmetrical vibrations of the NO_2 group[14] are clearly visible at 1350 and 1522 cm^{-1} as well as the absorptions of the aromatic group at 1263 and 1600 cm^{-1} (Figure 6b). The peaks of oxides are still visible, but those of carbonates seem to have disappeared. If the grafting is performed in 0.1 N sulfuric acid a very strong band is observed at 1180 cm^{-1} that can be due to either an increased oxide layer or the presence of sulfates; however, the signal of the NO_2 group can still be observed (Figure 6c).

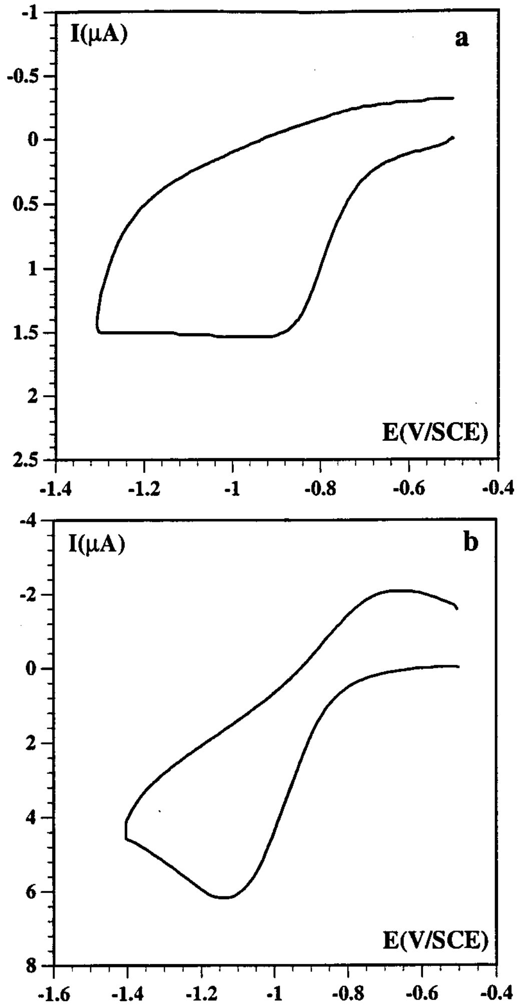

Figure 5. Cyclic voltammograms in an ACN + 0.1 M NBu_4BF_4 solution of a 3 mm iron electrode (a) which has been derivatized with anthraquinone groups (see text) and (b) in a 2 mM anthraquinone solution (the electrode has been previously immersed for 5 min in 0.1 N H_2SO_4 and then rinsed).

By using a 5 cm^2 glass plate covered by a thin layer of iron deposited by sputtering, it was possible to obtain a specular reflectance infrared spectrum of the organic layer obtained by reduction of the corresponding diazonium salt **12**. Figure 7 presents the IRTF spectra of the grafted benzoylphenyl groups and that of a reference spectrum of melted benzophenone.[15] Both spectra present very similar absorptions at respectively (i) 1659 and 1658 cm^{-1} (assigned[16] to the carbonyl group), (ii) 1317, 1278 and 1311, 1275 cm^{-1} (aromatic in-plane CH vibrations), and (iii) 1200−1000 cm^{-1} (rocking of the aromatic hydrogens). There are, however, differences between the two spectra: (i) the C=C stretching vibrations of the grafted benzoylphenyl groups are very weak and (ii) the spectrum of benzophenone shows out-of-plane CH vibrations at 762 cm^{-1} and an associated band at 698 cm^{-1} which are characteristic of monosubstituted benzenes. This last band disappears in the spectrum of the grafted groups while two new absorptions appear at 805 and 859 cm^{-1} which can be confidently assigned to CH out-of-plane

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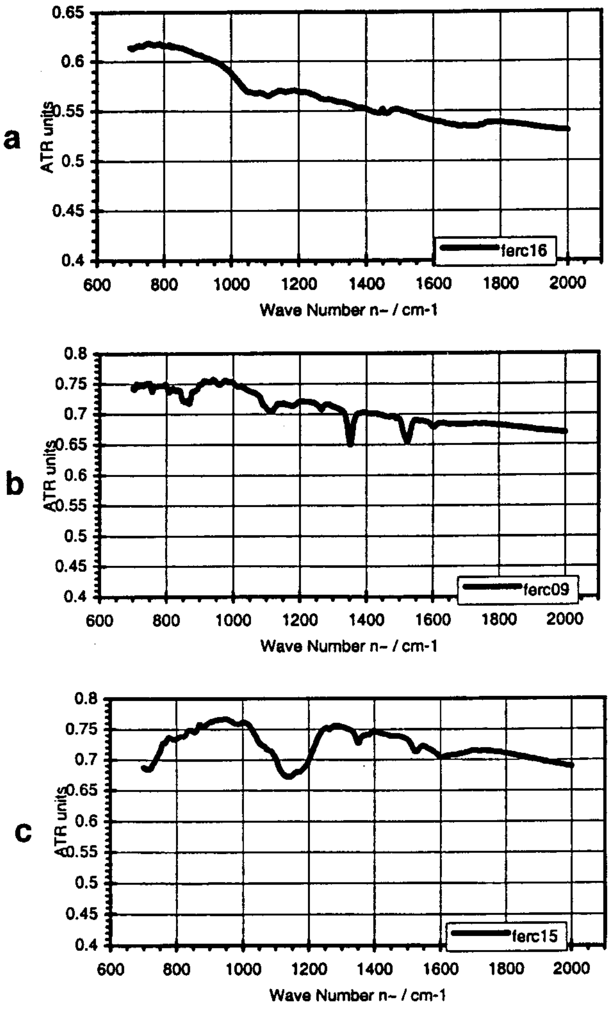

Figure 6. PMIRRAS spectra of mild steel plates (a) polished, (b) derivatized in ACN with 4-nitrophenyl groups, and (c) derivatized in 0.1 N H_2SO_4.

vibrations of 1,4-disubsituted benzenes. In addition, one can ascertain the loss of the diazonium group through the absence of any strong absorption in the 2000−2130 cm^{-1} region.[16b,c] Therefore this IR spectrum shows that during the electrochemical reduction the diazonium group has been lost and that one of the benzene rings remains 1,4-disubtituted in good agreement with the model of a benzoylphenyl group attached to the iron surface by the position para to the carbonyl group.

Rutherford Backscattering Spectra (RBS). This method measures the number of He^+ ions backscattered by the surface at a given energy, which permits the characterization of the elements and their surface concentration. The escape depth of the backscattered ions is of the order of the micron. It is necessary that the atomic number of the atom to be identified be about twice as large as that of iron to be differentiated. To fulfill this condition we derivatized carefully polished mild steel plates with 4-iodobenzene diazonium tetrafluoroborate. Figure 8 shows the RBS spectrum of such a plate after grafting in ACN. Table 1 shows the results of different experiments as a function of the solvent and potential. The only peak observed besides that of iron corresponds to the iodine atoms, which confirms the occurrence of the derivatization. Besides, analyses show that the grafting is homogeneous throughout the sample and stable under the ionic beam. In dilute sulfuric acid the optimum value of the potential is −0.75 V/SCE leading to the highest surface concentration; at more positive potentials the grafting comes into competition with the surface oxidation, and with the reduction of protons at more negative potential. The surface concentration will be discussed later.

X-ray Photoelectron Spectroscopy (XPS). It is worth noting that XPS and RBS are complementary surface analytical tools since the sampling depth of the former is about 2 orders of magnitude smaller than that of the latter. Figure 9 shows the wide XPS scans of a mild clean steel plate (Figure 9a) and 4-nitrophenyl- (Figure 9b), 4-carboxyphenyl- (Figure 9c), and 4-iodophenyl-treated mild steel (Figure 9d). All wide scans show $C_{[1s]}$, $O_{[1s]}$, and $Fe_{[2p]}$ peaks centered at ca. 285, 530, and 710 eV. Figure 9b shows a significant attachment of **1** following the electrochemical treatment of the mild steel plate. This is evidenced by a sharp increase in the relative intensity of $C_{[1s]}$ (see below) on one hand and a small peak around 400 eV. Enlargement of this region shows two peaks centered at 400 and 406 eV, the latter being due to the nitro group. The former may be due to some reduction products deriving from the diazonium salt.[5a] Note that the $O_{[1s]}$ peak was fitted with a component centered at 533 eV, a binding energy that is characteristic of the oxygen atom from a nitro group,[17] together with a second component at lower binding energy due to iron oxides. After reduction of 4-carboxybenzenediazonium tetrafluroborate **3** the spectrum of the steel plate presents a $C_{[1s]}$ peak at 289 eV (see below), a $O_{[1s]}$ signal fitted with two components at 531 and 532 eV assigned to the carbon and the C=O and OH oxygens of the carboxylic group, respectively, and a $F_{[1s]}$ peak around 690 eV due to some surface contamination by the BF_4^- ions of the electrolyte (Figure 9c). When the steel plate is modified with 4-iodophenyl groups the signal of the iodine atom can be observed at 621 eV (4.2%) (Figure 9d). The C/I ratio was 6.25, close to what is expected for a iodophenyl group. To ascertain that the presence of the attached group is not due to a mere adsorption or to a chemical reaction, the same steel plate, polished and cleaned as before, was dipped in a solution of **2** in ACN + 0.1 M NBu_4BF_4; under such conditions only a small signal (0.45%) of iodine was observed. This small signal can be due to a slow spontaneous reduction of **2** by iron as indicated at the beginning of this paper. It is worth noting that the attenuation of the $Fe_{[2p]}$ peak intensity by the overlayer for **1**, **2**, and **3** treated mild steel plates. There is also a noticeable increase in the noise level especially in the case of the attachment of **2**. The latter molecule seems to have a fairly complete coverage as the $Fe_{[2p]}$ doublet is no longer observed on the wide scan. The 700−1000 eV region characteristic of Fe Auger lines shows instead a noisy background due to increased inelastic energy loss.

As far as the $C_{[1s]}$ signals are concerned, we examined in detail those corresponding to nitrophenyl and carboxyphenyl groups attached to the surface by reduction of **1** and **3**, respectively (Figure 10), in order to determine if any part of the signal could be assigned to the carbon−metal bond. For nitrophenyl groups (obtained from **1**), $C_{[1s]}$ can be fitted with four components centered at 284.0, 285.0, 286.3, and 288.5 eV assigned to the metal-bonded carbon, aromatic carbons, $C-NO_2$ and/or C−O, and carboxylic carbons. The component assigned to the carboxylic groups is small and the origin of these groups is not clear. However, one must be aware that the main component due to the C−C/C=C has a relative intensity which exceeds that of the metal-bonded carbon. This, of course, makes peak fitting of the $C_{[1s]}$ very complex especially when one has

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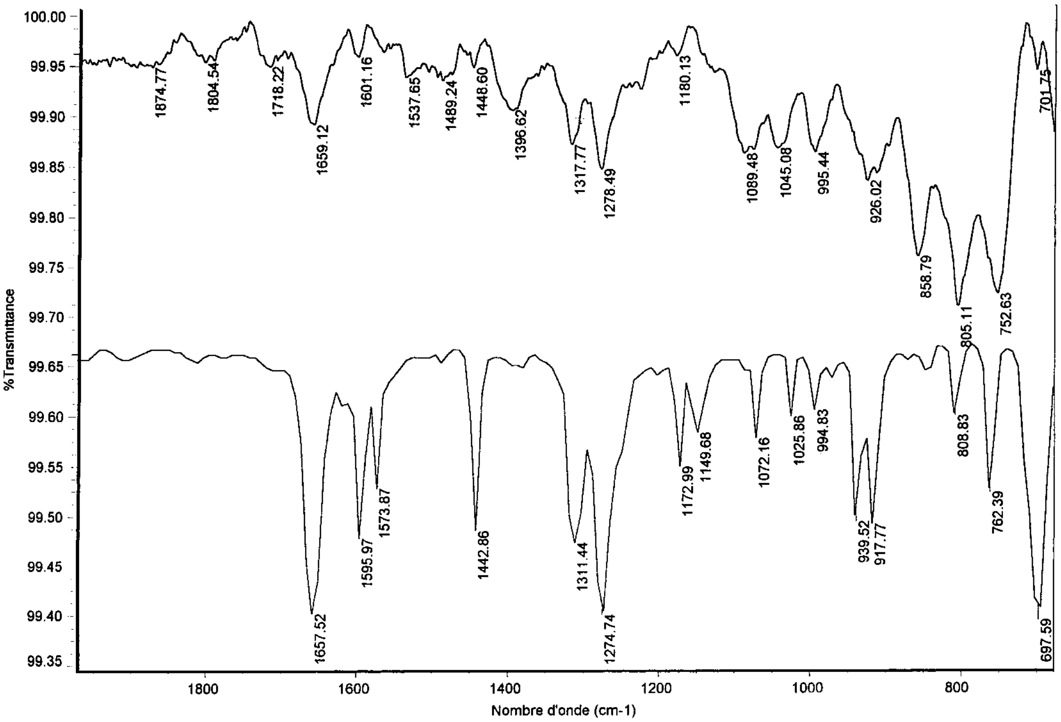

Figure 7. Reflection IRTF spectra of benzoylphenyl groups attached to the iron surface (top) and transmission IRTF spectrum of melted benzophenone (bottom).

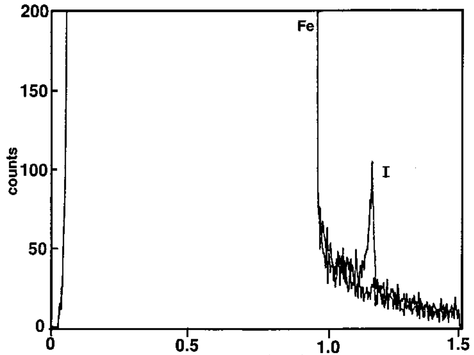

Figure 8. RBS spectrum of a mild steel plate modified (in ACN + 0.1 M NBu_4BF_4) with 4-iodophenyl groups.

to implement a low-intensity component at low-binding energy due to the C−metal bond. Nevertheless, the rationale for implementing such a component lies in the fact that the low-binding energy side of the $C_{[1s]}$ peak exhibits indeed a slight shoulder around a position corresponding to a carbide species. In the case of carboxyphenyl groups attached through the reduction of **3**, it is worth noting that the carboxylic group leads, as could be expected, to a much higher intensity of the apparent maximum around 288−289 eV. The $C_{[1s]}$ is fitted with five components as for nitrophenyl groups but with an additional component (288.6 eV) due to −*C*OOH. We also tentitatively fitted the whole $C_{[1s]}$ spectrum with a C−metal component at low binding energy (283.8 eV) that has an intensity comparable to that of −*C*OOH. The other components are assigned as indicated above for nitrophenyl groups.

XPS spectra were also utilized to find out whether the grafting was really taking place on iron or if the aryl group was bonded to the oxide which can always be present on that surface. Two steel plates were passivated in 1 N H_2SO_4 by sweeping the potential to +1 V/SCE (a potential located in the passive range of iron; passivation by the oxide layer can be observed by an increase of the oxygen peak from about 20% to about 40%), one of them was then dipped in a solution of **2** in ACN + 0.1 M NBu_4BF_4, while the other one was grafted as previously described in the same solution (a cathodic current is observed which shows that the oxide layer is not thick enough to block the electrode). In both cases only a small iodine signal was observed amounting respectively to 0.3 and 0.4%. This signal is much smaller than the signal observed after grafting on a polished and cleaned plate indicating that the aryl groups are bonded to iron and not to surface oxides.

Capacity of the Electrode. Attachment of an organic layer to the surface of the electrode should decrease the capacity of this electrode by adding a supplementary insulating layer in series with the electrochemical double layer. The capacity can be measured by an impedance method; we have recorded the Nyquist diagrams (Z_{Im} vs Z_{Re}) (Figure S2 in the Supporting Information). From the frequency of the maximum, it is possible to obtain C_d.[18] The capacity of a 3 mm diameter pure iron electrode in 0.1 N H_2SO_4 was found to be 334 $\mu F/cm^2$. After modification of the electrode surface with 4-hexadecyloxy groups (by reduction of diazonium **8** in 0.1 N H_2SO_4), the capacity falls to 192 $\mu F/cm^2$.

Surface Concentration of the Attached Groups. Two methods can be used to measure the surface concentration of aryl groups. The first one involves the measurement of the charge used to reduce by one electron per molecule the nitro groups bonded to the surface (after thorough rinsing of the electrode and transfer to an ACN + 0.1 M NBu_4BF_4 solution). This amounts to the integration of the voltammogram recorded from an electrode modified with nitrophenyl groups.[1] One of the drawbacks of such a method is that it necessitates the estimation of a baseline and of the end point of the voltammogram. The second method relies on the integration of the RBS spectra; in this case one must be certain that only the grafted area of the electrode is included in the beam and that the surface

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[18] Bard, A. J.; Faulkner, L. J. *Electrochemical Methods*; J. Wiley: New York, 1993; p 345.

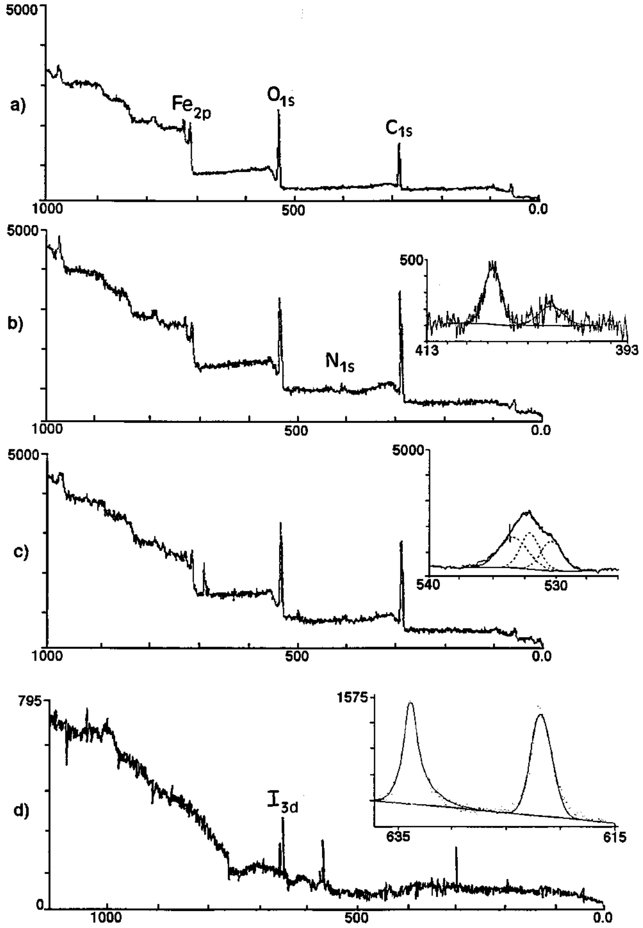

Figure 9. XPS spectra of (a) a clean mild steel plate and (b) of a mild steel plate derivatized with 4-nitrophenyl groups, (c) with 4-carboxyphenyl groups, and (d) with 4-iodophenyl groups.

is stable under the ion beam. Both methods provide values related to the geometrical surface (i.e. 1 cm^2 for a 1 × 1 cm plate) of the electrode previously polished with 1 μm diamond paste. The values in Table 1 provide results which, for similar conditions, are in fair agreement. For example, grafting of 4-nitrophenyl or 4-iodophenyl groups of similar size led to similar surface concentrations and increasing the size of the attached group from 4-nitrophenyl to anthracenyl or anthracenyl-9,10-dione decreases the surface concentration. Surface concentrations obtained in dilute sulfuric acid reach at most 67% of that obtained in ACN. This may be due to the oxidation of the surface in sulfuric acid which decreases the surface available for bonding aryl groups or to hydrogen formed on the surface or adsorbed in the metal,[19] which would change the properties of the surface and prevent the electrochemical reaction. The above surface concentrations can be compared with those previously measured on carbon and particularly on HOPG (the real surface of which is very close to the geometrical surface). The surface concentrations of 4-nitrophenyl groups which have been measured[1,2] lie in the range (12−18) × 10^{-10} mol/cm^2; however, on glassy carbon, polished under the same conditions as the iron electrodes, or steel plates used in this paper, a value of 40 × 10^{-10} mol/cm^2 was obtained after reduction of **1**. Therefore, there is good agreement between the values obtained on carbon and that on iron or steel. This was confirmed by recording the chronopotentiometric curves ($E = f(t)$ at constant current). For the grafting of **5** the first transition time corresponds to the reduction of the diazonium function. Nearly identical transition times were obtained for iron and carbon polished in the same way. This indicates that the same amount of charge is needed to achieve complete coverage of the electrode up to the time where the diazonium is no longer reduced on the electrode. On HOPG such surface concentrations have been shown to correspond to a closed-packed monolayer of aryl rings standing up on the surface[1] (a stereochemical situation where 4-iodo- and 4-nitrophenyl groups occupy the same surface and anthracenyl groups a larger one).

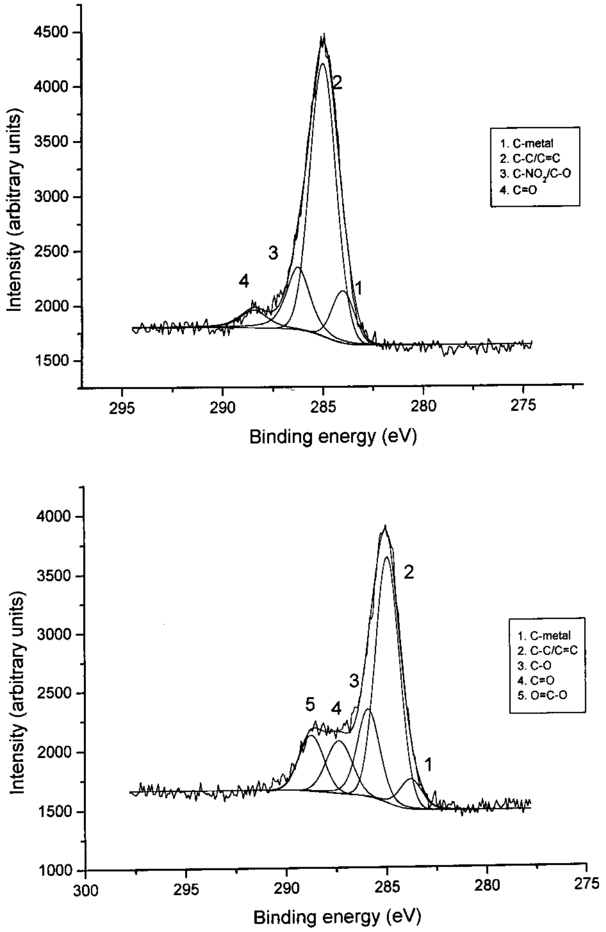

Figure 10. XPS spectrum of the C$_{[1s]}$ peak of 4-nitrophenyl groups (upper) and 4-carboxyphenyl groups (lower) attached to an iron surface.

Table 1. Surface Concentration of Aryl Groups[a]

sample[b]	solvent[c]	electrolysis potential, V/SCE	method of measurement	surface concn, mol/cm^2 [a]
iron +**1**	ACN	−0.85	VC	45 × 10^{-10}
iron + **11**	ACN	−0.85	VC	12 × 10^{-10}
iron + **12**	ACN	−0.85	VC	8 × 10^{-10}
steel +**2**	ACN	−0.85	RBS	48 × 10^{-10}
steel +**2**	0.1 N H_2SO_4	−0.75	RBS	32 × 10^{-10}
steel	0.1 N H_2SO_4	−0.75	RBS	0

[a] Surface concentration per geometrical surface. [b] Material of the electrode + diazonium salt used for derivatization. [c] Used for derivatization.

Atomic Force Microscopy (AFM) Imaging of the Surface. Figure S3 (Supporting Information) shows the AFM images of a mild steel surface that has been (a) carefully polished with 1 μm diamond paste and ultrasonically rinsed for 20 min in acetone, (b) maintained in ACN + 0.1 M NBu_4BF_4 at −0.85 V/SCE for 30s, and (c) grafted by 4-*n*-butylphenyl groups

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(19) O'M. Bockris, J. *Surface Electrochemistry*; Plenum: New York, 1993; pp 745−852.

(through reduction of **4**) in the same medium, at the same potential for the same time. The polished surface (Figure S3a) appears rather smooth with parallel grooves made by the diamond grains as well as some small particles typically 20 nm high which can be either iron or diamond particles that are not removed from the surface by ultrasonic rinsing. Figure S3b does not show significant changes by comparison with Figure S3a, indicating, as could be expected from the $i = f(E)$ curves, that no corrosion is taking place. Except for the particles initially present on the surface, Figure S3c shows a homogeneous surface where the grooves are still visible. The roughness of the surface was measured: R_a varies from about 2 nm for Figure S3 (a and b) and increases to only 3 nm upon grafting. The fact that no significant change can be observed by AFM rules out the existence of a nanometers thick polymeric layer but does not exclude the formation of a multilayer (molecular models show that a bilayer, obtained by substitution ortho to the butyl group, of *n*-butylphenyl groups would not be thicker than a monolayer, ∼9.7 Å).

Discussion and Conclusion

We have shown that the electrochemical reduction of diazonium salts on an iron or steel electrode leads to strongly bonded aryl groups on the iron surface. Although this reaction should be thermodynamically possible without electrochemical activation, it is too slow to occur to a significant extent as was demonstrated by XPS experiments. The existence of attached aryl groups was evidenced by cyclic voltammetry, XPS, PMIRRAS, RBS, and capacity measurements. These different methods rely on different physical principles; their combined use and the convergent results obtained give confidence in the reality of the grafting. XPS, FTIR, and PMIRRAS permit qualitative characterization of either the atoms or the functional groups; cyclic voltammetry and RBS provide quantitative data on the surface concentration. Comparison with the data obtained on carbon points to the formation of a monolayer, which is also supported by AFM measurements that show no evidence for the formation of a nanometer thick polymer layer. As iron is very easily oxidized in contact with atmosphere or in aqueous acidic solution, one could wonder whether an O−aryl bond is formed instead of an Fe−aryl bond, but we have seen above that XPS measurements indicate that the grafting on a purposely oxidized surface is negligible. Another point that should be discussed is the nature of the Fe−aryl bond. The grafting resists ultrasonic rinsing in a variety of solvents and for long periods of time but also several days of rinsing in boiling toluene. This makes a mere adsorption unlikely. An ionic bond between Fe^{2+} or Fe^{3+} and an aryl carbanion is also highly unlikely, as aryl carbanions are very strong bases which would be readily protonated even in ACN. Therefore one must conclude the existence of a covalent Fe−aryl bond; such bonds are known in organometallic chemistry,[20] for example, the compound $FeArCp(CO)_2$ ($Ar = C_6H_4CH_3$ and $Cp =$ cyclopentadienyl) has been prepared and fully characterized. This is also supported (i) by the observation of a shoulder at low binding energy on the $C_{[1s]}$ peak which was assigned to a component corresponding to the carbon bonded to the metal and (ii) by the observation of a 1,4-substitution pattern on the FTIR spectrum of attached benzoylphenyl groups.

The grafted organic layer provides some protection of the mild steel surface against corrosion; the inhibition efficiency I.E. $= 100(1 - i_{corr}^{graft}/i_{corr})$ reaches 82% for 4-butylphenyl groups (by reduction of **5**) in 5% KCl and 77% for dodecyloxy groups (by reduction of **7**) in 0.1 N H_2SO_4. These inhibition efficiencies correspond to the values which can be observed when inhibitors such as alkynols and triazoles are added in solution.[17,21,22] But starting from mild steel plates derivatized as described in this paper it was possible to attach micrometer thick polymeric layers which completely block the surface.

The formation of an organic layer covalently bonded to an iron surface is not entirely unprecedented; the only similar process of which we are aware has been described by G. Lecayon and co-workers. Metallic surfaces such as Fe, Ni, Pt, and Au have been covalently modified by electrochemical reduction of vinylic monomers such as acrylonitrile, methacrylonitrile, and butenenitrile. Thin polymeric layers (≈10−50 nm) covalently bonded to the metal are obtained, the structure of which have been thoroughly investigated.[23−25] Protection of metal from corrosion by this process has proved to be quite efficient.[25] The older investigations of Elofson and Gadallah[26] should also be quoted; they had investigated the reduction of diazonium salts on mercury electrodes and they had used the radicals obtained in this way for further cyclization reactions, but they also found the formation of aryl mercury compounds which are analogues of the aryl groups attached to the iron surface.

Many possible applications can be imagined for this process, including the protection of iron against corrosion, the improvement of adhesion between organic or polymeric layers and iron, or the formation of iron surfaces with specific properties in the biomedical field; it is indeed one of the characteristics of this process that the organic groups which can be attached to the iron surface can be varied at will and can be used as a further a starting point for chemical reactions.

Further experiments are now in progress which show that the process can be extended to other engineering (Zn, Cu, Ni, Co) and coinage metals (Au, Pt).

Experimental Section

Chemicals, Electrodes. ACN was obtained from Merck (Uvasol), H_2SO_4 from Prolabo (Tritrinorm), and NBu_4BF_4 from Fluka (puriss.). Diazonium salts **1** and **11** are of commercial origin (Aldrich) and the synthesis of **3** has been previously described;[1c] **2**, **3**−**6**, **9**, **10**, and **12** were obtained from the corresponding commercial amines by standard methods.[27] The diazonium salts were kept in a freezer before use.

4-Iodobenzenze diazonium tetrafluroborate 2:[28] mp 126 °C (lit. mp 123−124 °C); ^1H NMR (200 MHz, DMSO) δ 8.4 (q, 4H, aromatics).

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4-Methylbenzenze diazonium tetrafluoroborate 4:[30] mp 110 °C dec (lit. mp 110 °C dec); ^{1}H NMR (200 MHz, DMSO) δ 2.5 (q, 3H, CH_3), 7.8−8.5 (two d, 4H, aromatics).

4-*n*-Butylbenzenediazonium tetrafluoroborate 5:[28] In an Erlenmeyer flask placed in an ice bath, 4-*n*-butylaniline (149 mg, 1 mmol) is dissolved in HBF_4 (34%, $d = 1.23$, 3 mmol, 30 mL) and stirred for 15 min, then $NaNO_2$ (1.5 mmol, 103 mg) is added. The mixture is stirred for 20 min. CH_2Cl_2 (30 mL) is then added and the organic and aqueous layers are separated in a separatory funnel. The organic phase is dried over $MgSO_4$ and evaporated to give a pale yellow solid. No melting point could be measured as described in the literature.[28] ^{1}H NMR (200 MHz, DMSO) δ 0.9 (t, $^3J = 6$ Hz, 3H, CH_3), 0.8−2.8 (m, 5H, CH_2), 2.8 (t,$^3J = 8$ Hz, 2H, CH_2 benzylic), 7.6−8.5 (q, $^3J = 8$ Hz, 4H, aromatics).

4-*n*-Dodecylbenzenediazonium tetrafluoroborate 6:[30] mp 70 °C dec; ^{1}H NMR (200 MHz, DMSO) δ 0.85 (t, $^3J = 6$ Hz, 3H, CH_3), 1.1−2.8 (m, 20 H, CH_2), 2.5 (t,$^3J = 8$ Hz, 2H, CH_2 benzylic), 7.8−8.5 (q, $^3J = 8$ Hz, 4H, aromatics).

7 was prepared from 4-dodecyloxyaniline[31] as described before: white solid, ^{1}H NMR (200 MHz, DMSO) δ 0.8−1.8 (m, 25H, aliphatic protons), 4.3 (t, 2H, O−CH_2), 7.5−8.5 (q, $^3J = 8$ Hz, 4H, aromatics).

8 was prepared in a similar way but the diazonium salt still contained some amine: white solid, ^{1}H NMR (200 MHz, DMSO) δ 0.8−1.8 (m, 33H, aliphatic protons), 4.2 (t, 2H, O−CH_2), 7.2−8.5 (q, $^3J = 8$ Hz, 4H, aromatics).

Electrodes were prepared either from 1 mm diameter iron wire (Johnson-Matthey 99.99%) embedded in epoxy resin or from 3 mm diameter mild steel buttons maintained in a Teflon holder. Mild steel plates (containing Fe 95.68%; C 0.31%; Mn 2.03%; P 0.05%; S 0.13%; N 0.56%; Si 0.10%; Cu 0.07%; Ni 0.18%; Cr 0.30%; Sn 0.01%; Al 0.58%) were kindly given by the Société Sollac.

Electrochemical Equipment. Electrochemical curves were obtained either with a homemade potentiostat or a Versastat II from EGG (Priceton Applied Research). Impedance measurements were obtained with an EGG potentiostat 263A and a lock-in amplifier 5210. The frequencies investigated ranged from 0.001 Hz to 20 kHz and corrosion currents were obtained from the Tafel plots with the EGG corrosion software without ohmic drop compensation.

Surface Characterization. XPS, PMIRRAS, and RBS equipment and conditions have been described previously.[1c] Elemental percentages x_i were obtained from $x_i = (A_i/S_i/\sum_i(A_i/S_i)$, where A_i and S_i are respectively the peak area of the detected element and the sensitivity coefficient deduced from the study of the stoichiometric coefficient. AFM images were obtained with a Nanoscope III. A series of reproducible images were obtained from which we have selected that of Figure S2. The average surface roughness expressed in nm, was calculated by using the manufacturer's software according to:

$$R_a = \frac{1}{L_x L_y} \int_0^{L_x} \int_0^{L_y} |f(x,y)|\, dx\, dy$$

L_x and L_y are the dimensions of the surface and $f(x,y)$ is the surface relative to a calculated flat plane based upon the surface data that has equal volume above and below the plane.

Acknowledgment. We acknowledge the help of Mrs. Carole Bilhem and Pascal Bargiela (ITODYS) for recording the XPS spectra and of Dr. Mohammad Bousmène for permission to use his electrochemical corrosion equipment. We are grateful to M. Gruselle (Laboratoire de Synthèse des Composés Organométalliques, Université Pierre et Marie Curie) and to Dr. O. T. Yurevna (INEOS Institute, Academy of Sciences, Moscow) for the gift of the product $FeArCp(CO)_2$. The $C_{[1s]}$ spectra were fitted with the Winspec software kindly provided by Dr. Pierre Lovette (Lise, Namur, Belgium).

Supporting Information Available: Figure S1 showing the cyclic voltammogram of anthracene on an iron electrode and of an iron electrode modified with anthracenyl groups; Figure 2 showing the impedance diagram in 0.1 N H_2SO_4 of an iron electrode before and after modification by hexadecyloxyphenyl groups; and Figure S3 showing AFM images of mild steel plates before or after derivatization (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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