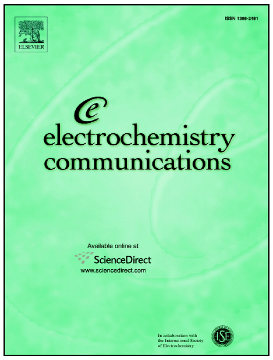

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# Electrode grafting by oxidation of an amine catalyzed by a ferrocenyl "antenna" through intramolecular electron transfer

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## ABSTRACT

Two aminoferrocene complexes were studied by electrochemical techniques. Molecules retain the redox properties of both ferrocene and amine groups, but fundamentally different behaviours were observed depending on whether the linker between the two redox end groups was saturated (ethyl bridge) or not (ethynyl bridge). The possibility of an intramolecular electron transfer from the amine to the ferricenium moiety through the π-conjugated linker was demonstrated and the ethynyl bridge is expected to have a dual effect by facilitating both the oxidation of the amine into the cation radical and the production of aminyl radical, due to its strong electron withdrawing effect. Because of this synergy of properties, grafting of the conjugated aminoferrocene complex can occur just by oxidizing the ferrocene group without the presence of a base in solution.

KEYWORDS. MODIFIED ELECTRODE, FERROCENE, AMINE, INTRAMOLECULAR ELECTRON TRANSFER, RADICAL AMINYL

## INTRODUCTION

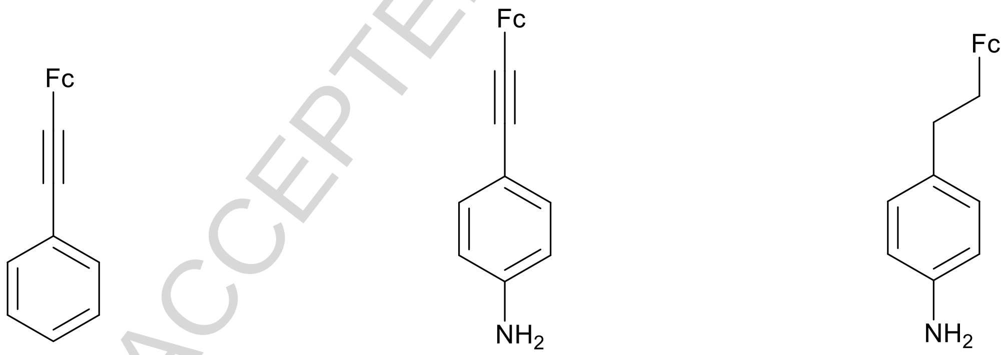
Amine is a key surface attachment functionality to prepare modified surfaces for sensor applications due to its presence in a wide variety of biomolecules. Particularly, primary amines give a radical cation upon oxidation and after deprotonation, favoured by the presence of a base in solution, the radical aminyl obtained can react with carbon and metallic surfaces to be covalently attached [1]. Unfortunately, due to the poor delocalization of the charge in the amino cation-radical, the oxidation of aliphatic amines occurs most often beyond 1 V/SCE, that is hardly accessible in physiological media [2]. Because of a better delocalization of the charge, the oxidation of aromatic primary amines becomes easier and grafting is possible in aqueous media [3]. Recently, a conjugated amino-ferrocifen complex could even be grafted at very low potential, by oxidizing the ferrocene (0.4 V/SCE) through an intramolecular electron transfer from the amine to the ferricenium moiety acting as a redox shuttle [4,5]. Here, we studied the electrochemical behaviour of two aminoferrocene complexes, having saturated and unsaturated bridges, in order to demonstrate the impact of the conjugation on the grafting efficiency. Computational modelling and electrochemical techniques were applied to gain insight into the behaviour of molecules following the one-electron oxidation of the ferrocene moiety, while electrodes modified at different potential values were investigated by X-RAY PHOTOELECTRON SPECTROSCOPY (XPS) AND ATOMIC FORCE MICROSCOPY (AFM) EXPERIMENTS.

## EXPERIMENTAL SECTION

**REAGENTS AND SURFACES.** TETRABUTYLAMMONIUM HEXAFLUOROPHOSPHATE (ALDRICH) AND ACETONITRILE (HPLC GRADE, CARLO ERBA) WERE USED AS RECEIVED. GLASSY CARBON (GC) ELECTRODES FROM BIOANALYTICAL SYSTEMS INC. (MODEL MF-2012; 3 MM IN diameter) were used for cyclic voltammetry and controlled-potential electrolysis. GC sheets were used for XPS and PPF samples for AFM.

### Synthesis of ferrocenyl compounds.

The ferrocenyl arylethyne and arylethyl compounds (scheme 1) were synthesized by Sonogashira coupling of ethynylferrocene with the iodobenzene (1), 4-iodoaniline (2) and 1-iodo-4-nitrobenzene followed by hydrogenation of the ferrocenyl-nitrobenzene compound with Pd/C 10% under $H_2$ at room temperature for 24h (3). In all cases, ethynyl-ferrocene, iodoaryl compounds (1 equiv.) and catalytic amounts (5 mol %) of $Pd(PPh_3)_2Cl_2$ and CuI were reacted in diisopropylamine (20 mL) under argon at 50°C for 24h. The catalyst was removed by filtration through a short pad of Celite, and the filtrate was washed with 10 mL of water and extracted with 20 mL of dichloromethane. After evaporation, the residue was purified using chromatography on $SiO_2$ with a petroleum ether/dichloromethane eluant to afford 1, 2 and 3 as a red, orange and yellow solid, respectively.



Phenylethynylferrocene (**1**) 4-(ferrocenylethynyl)aniline (**2**) 4-(2-ferrocenylethyl)aniline (**3**)

Scheme 1: The ferrocenyl compounds studied.

### Instrumentation and procedure

Electrochemical measurements were achieved in a three-electrode cell containing acetonitrile + 0.1 M $nBu_4NPF_6$. The counter electrode was a platinum wire and the working electrode was a GC or a PPF electrode depending on the experiment. All potential values are referred to the Fc$^{+/0}$ redox couple. A potentiostat/galvanostat model VSP (from Bio-Logic) monitored by ECLab software was used. For the surface characterization experiments, carbon electrodes were sonicated for 10 min in acetonitrile before to be studied.

XPS measurements were performed with a Kratos Axis Ultra spectrometer using a Al K$\alpha$ monochromatic beam working at 1486.6 eV. All spectra were recorded in the constant energy mode at a pass energy of 20 eV. Data treatment was performed with CasaXPS software and all spectra were calibrated taking 284.5 eV (graphite-like carbon) as a reference binding energy.

AFM studies were carried out using the NanoObserver microscope from CSInstruments in tapping mode. The acquired images were processed with the Gwyddion free SPM data analysis software. The thickness of the deposited layer on PPF was calculated from the profile obtained by scratching the surface with the AFM tip.

For all calculations the Gaussian 09 software (revision A.02) was used. The geometries of molecules were optimized after the charge reorganization following the first one-electron oxidation with the density functional theory (DFT) using the PBE0 hybrid function. Atomic charge mapping was obtained by Hirshfeld population analysis of density functional electronic charge distributions calculated from the 6-311+G(2df,2pd) basis set.

## RESULTS AND DISCUSSION

Recently, multicomponent molecular assemblies incorporating the ferrocenyl group as an electron donor were extensively used to explore the intramolecular electronic interactions in donor-acceptor conjugated systems suitable for nonlinear optical (NLO) materials, metal ion recognition applications and electrode surface modifiers [6]. Regarding this latter issue, we have studied the electrografting efficiency of two ferrocenyl-aniline derivatives having a saturated or unsaturated spacer. Figure 1 presents the cyclic voltammograms (CVs) of molecules in acetonitrile solution and the computational modelling of the two aminoferrocene complexes upon the first one-electron oxidation.

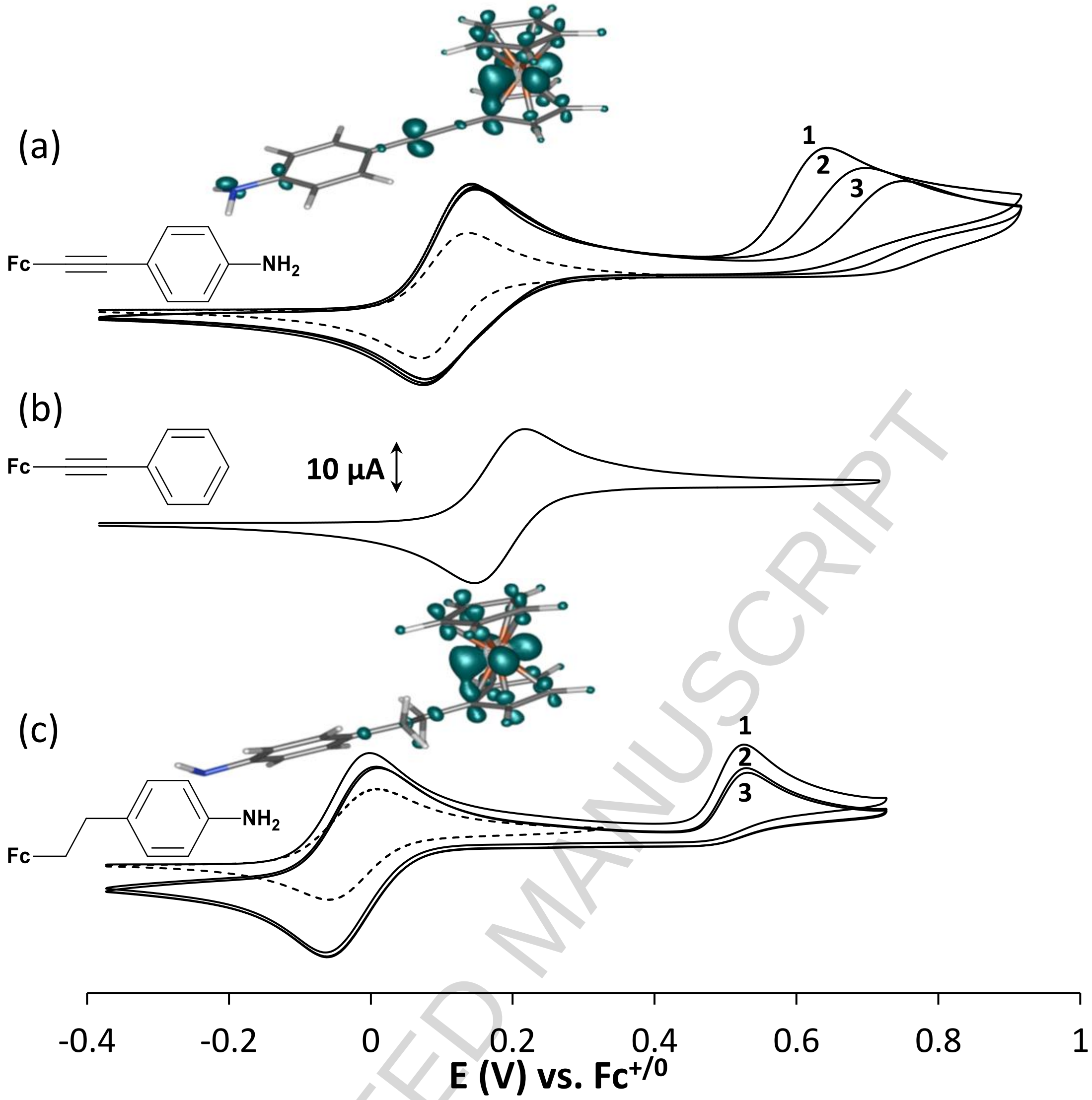


FIGURE 1

The two aminoferrocene complexes retain the redox characteristics of both ferrocene and amine groups, with features of reversible and irreversible one-electron transfers. When the ferrocene and the amine groups are connected through a saturated bridge, the formal potential of the ferrocene, $E^{\circ}_{Fc}$, is almost independent of the aminophenyl ring ($E^{\circ}_{Fc}$ = - 0.019 V). However, this potential is centered at $E^{\circ}_{Fc}$ = 0.112 V for the CONJUGATED-BRIDGED AMINOFERROCENE COMPLEX, THAT IS NEGATIVELY SHIFTED compared to the phenylethynylferrocene ($E^{\circ}_{Fc}$ = 0.184 V), demonstrating an intramolecular interaction between the two redox-end groups. In addition, when consecutive CVs were recorded in the CONJUGATED-BRIDGED AMINOFERROCENE solution, a rapid decrease of the oxidation wave of the amine was obtained, in good agreement with the electrode passivation by attack of aminyl radicals.

By analogy, consecutive CVs obtained with the SATURATED-BRIDGED AMINOFERROCENE derivative show a better stability, and the presence of 2,4,6-trimethylpyridine (collidine) as a base was needed to passivate the electrode surface by facilitating the deprotonation of the electrogenerated amino cation-radical into the aminyl radical (results not showed). These results demonstrate that the ethynyl bridge have the dual effect of improving the electronic contact between the two redox-end groups and fostering the production of aminyl radicals by facilitating the deprotonation of the amino cation-radical due to its strong electron withdrawing nature. In addition, the theoretical modelling of the charge distribution occurring in the aminoferrocene complexes following the one-electron oxidation of the ferrocenyl moieties, shows the presence of a fraction of positive charge density on the nitrogen atom when an ethynyl bridge exist (Figure 1), implying an intramolecular electron transfer from the amine to the electrogenerated ferricenium moiety. Nonetheless, the intra-molecular electron transfer is assumed to be very slow, since the oxidation of the ferrocenyl moiety for the π-conjugated aminoferrocene complex remains reversible in the cyclic voltammetry time-scale even at 50 mV/s (CVs in dotted line in Figure 1).

Under such conditions, the attachment of the aminoferrocene complex could occur via the oxidation of the ferrocene group. To verify this assumption, a GC electrode was polarized for 5 min at different potential values in 1 mM aminoferrocene acetonitrile solutions. After thorough rinsing, the GC electrode was transferred in a free acetonitrile solution to be studied. Figure 2 presents the relation between the electrode surface coverage, determined by integrating the CV recorded at 100 mV/s in acetonitrile, and the electrode potential. Typical CVs recorded in acetonitrile for electrodes polarized at 0.027 V, 0.927 V and at potential values corresponding to maximum surface coverages, are superimposed.

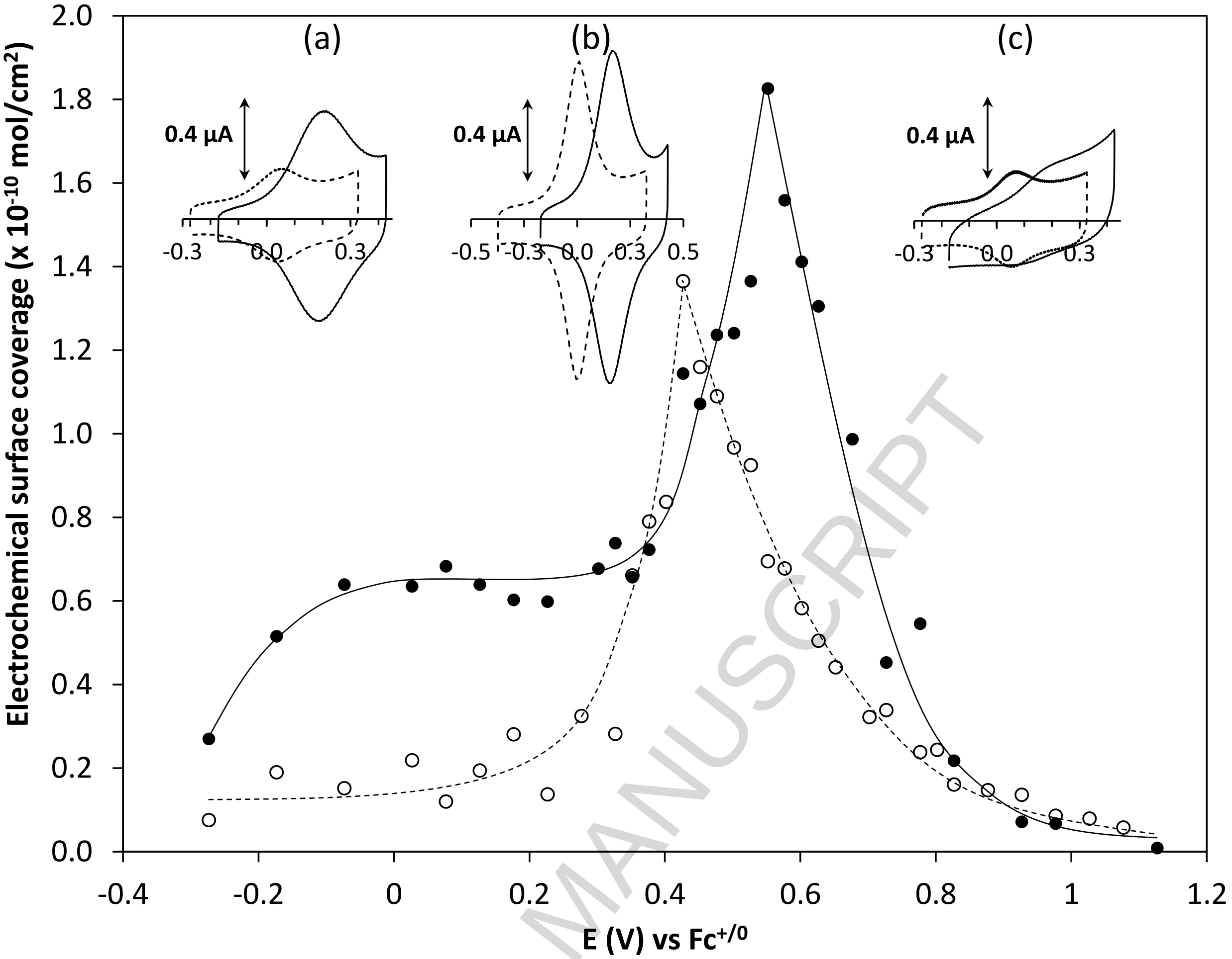


FIGURE 2

Importantly, after electrolysis at potential values where only the ferrocene group was oxidized, GC electrodes were solely modified when an unsaturated bridge exists. In this low-potential range, the electrode coverage was found equal to ca. 0.6 x $10^{-10}$ mol/cm$^2$ for the CONJUGATED-BRIDGED AMINOFERROCENE, compared to ca. 0.1 x $10^{-10}$ mol/cm$^2$ for the saturated derivative, which can be attributed either to an inefficient electron transfer through the saturated bridge or to a spontaneous nucleophilic addition of the amine on the carbon surface. Note that CVs recorded on modified electrodes show a peak-to-peak potential separation minus than 20 mV at 100 mV/s, that agrees well with surface-confined molecules. In addition, the fact that the potential offset for the response of the ferrocenyl attached complexes is maintained, proves that the ethynyl bridge is preserved during the grafting. These results are in good agreement with those obtained by Amatore et al. with a conjugated amino-ferrocifen complex, for which the grafting was possible from the oxidation of the ferrocene [4,5].

When the amino groups start to be oxidized, the electrode coverage rapidly increases to a maximum, exceeding a surface coverage of 1.3 x $10^{-10}$ mol/cm$^2$, before decreasing dramatically, falling nearly to zero beyond 1 V. For the conjugated aminoferrocene complex, the net increase in the electrode coverage when GC electrode is polarized at the threshold potential of the oxidation of the amine indicates that the grafting process is more efficient when the amino group is directly oxidized. However, the rapid decrease in the surface coverage for applied potential values exceeding that of the amine remains unclear. This sudden drop in redox activity is inconsistent with a progressive electrode passivation resulting in the growth of a poorly conducting organic layer, and by analogy with a recent work, we tentatively suggest that the organic layer generated in this high-potential range totally blocks the electrode in the potential window investigated [7].

For a better surface characterization, XPS and AFM experiments provide information on the film composition and its “dry state” thickness, depending on the potential applied (Figure 3). In order to obtain unambiguous results, longer electrolysis (one hour) in concentrated solutions (5.9 mM) were performed. As demonstrated by depth profiling achieved on modified PPF working electrodes by scratching a small section of attached films with an AFM tip, multilayer films were obtained with the unsaturated-bridged ferrocene complex by direct or indirect oxidation of the amine (Figures 3B and 3C). By contrast, when the spacer group is saturated, only the direct oxidation of the amine gives a multilayer film (Figure 3F). In these experiments, the three lowest depth profiles are assumed to be due to non-radical electrochemically induced reactions, such as spontaneous nucleophilic addition of the amine. In the current state of our knowledge, it seems to us to be hazardous to compare and discuss the thicknesses of grafted films, because a strong heterogeneity was observed in a similar study [5]. However, the main conclusion is that a multilayer film can be obtained by oxidizing the ferrocenyl moiety of the unsaturated-bridged ferrocene complex, confirming the possibility of an indirect oxidation of the amine.

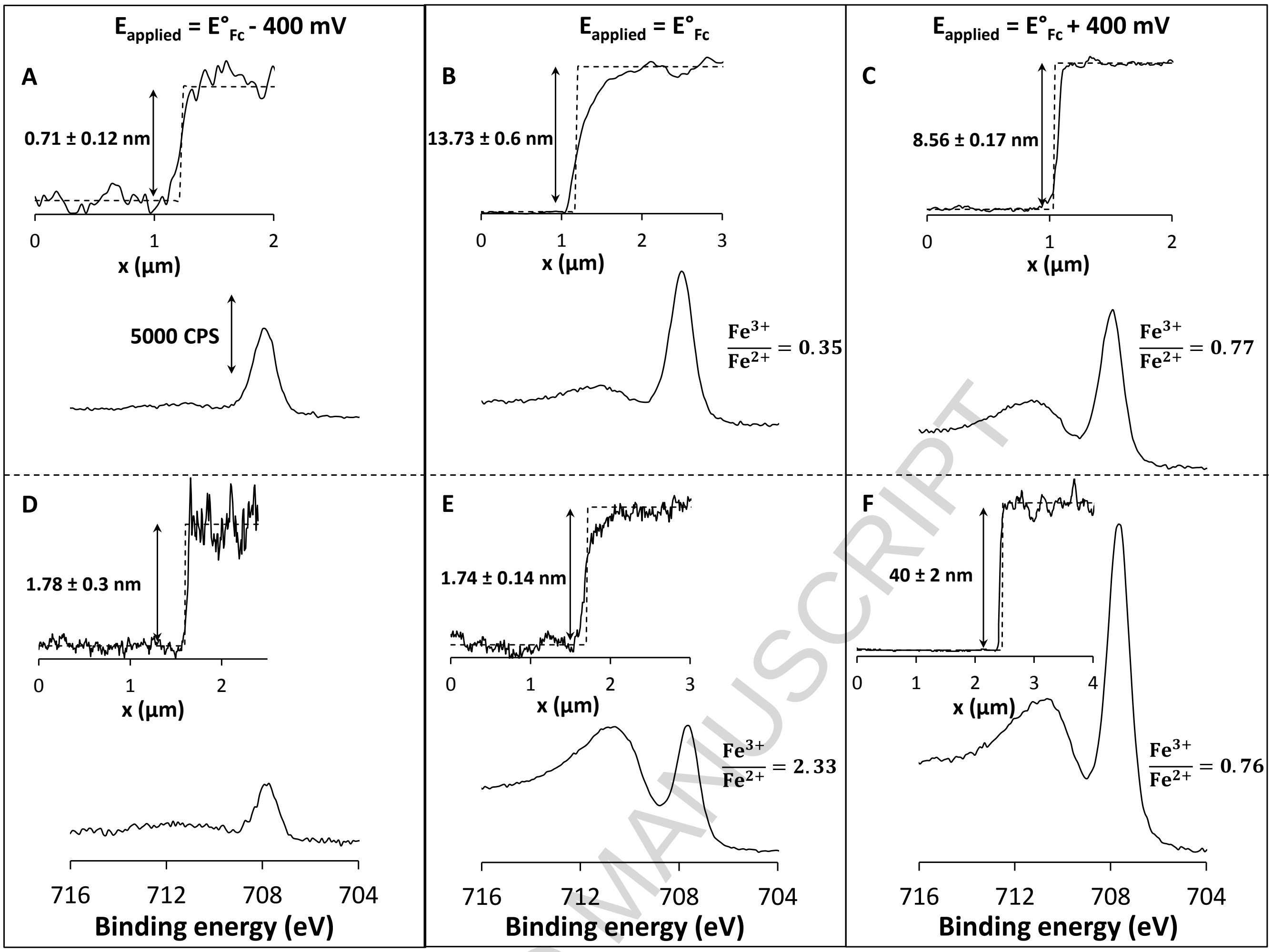


FIGURE 3

XPS spectra of Fe $2p_{3/2}$ core levels as a marker of molecules in the grafted films, and especially the Fe(III)/Fe(II) atomic ratio, is very instructive about the intramolecular redox process (Figure 3). When GC sheets were assumed to be just spontaneously modified (Figures 3A, 3D and 3E), the XPS spectra consist mainly in a peak ascribed to Fe(II) (at 707.9 eV) or Fe(III) (at 711 eV), according to the GC sheet is biased at a potential where the ferrocenyl moiety is in its reduced or oxidized form. In contrast, it is noteworthy that the ferrocenyl moiety is attached to the surface in mixed valence states when multilayer films were obtained, even though the GC sheets were biased at potential values where the ferrocenyl group is oxidized. In such cases, the existence of ferrocene in reduced form may be explained by the ferricenium reduction via an intramolecular electron transfer from the amine (Figure 3B) or by reaction of the ferricenium moiety with a radical species, giving a substituted ferrocene [8]. The present results do not distinguish between these two mechanisms and further experiments designed to probe this question are in hand.

## CONCLUSION.

A conjugated aminoferrocene complex has been grafted on carbon electrodes at a low potential and without a base in solution by indirect oxidation of the amine via the ferrocene group acting as a redox shuttle. The presence of Fe(II) in the XPS spectra and evidence of a multilayer film produced at the formal potential of the ferrocene point towards an intramolecular electron transfer from the amine to the ferricenium moiety.

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## FIGURE CAPTIONS

**Figure 1:** CVs recorded on a GC electrode at 100 mV/s (solid lines) and 50 mV/s (dotted lines) in 1 mM acetonitrile solutions of 4-(ferrocenylethynyl)aniline (a), phenylethynylferrocene (b) and 4-(2-ferrocenylethyl)aniline (c). Computational modelling of the charge distribution following the first one-electron oxidation was superimposed for the two aminoferrocene complexes.

**Figure 2:** Relation between surface coverage and electrode potential during micro controlled potential electrolysis achieved in 1 mM acetonitrile solutions of 4-(2-ferrocenylethyl)aniline (empty circles) and 4-(ferrocenylethynyl)aniline (full circles). Typical CVs for GC electrodes modified with 4-(ferrocenylethynyl)aniline (solid lines) and 4-(2-ferrocenylethyl)aniline (dotted lines) at 0.027 V (a), at the potential values corresponding to the maximum surface coverages (b) and at 0.927 V (c), were presented.

**Figure 3:** Fe 2p core levels XPS spectra of modified GC sheets and depth profiling achieved by AFM on PPF surfaces polarized at potential values specified in the figure for 1 h in 5.9 mM acetonitrile solutions of 4-(ferrocenylethynyl)aniline (A-C) and 4-(2-ferrocenylethyl)aniline (D-F). Note that $E^{\circ}_{Fc}$ is defined as the geometric average of the peak potentials of the reversible ferrocene/ferricenium couple.

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## HIGHLIGHTS

- An intramolecular electron transfer from an amine to a ferricenium moiety is demonstrated
- A ferrocenyl ‘antenna’ makes it possible to graft an amino compound at low anodic potential
- Preparation of surface molecular assemblies of unsaturated bridged ferrocenyl moieties