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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.

1. 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.

2. Experimental section

2.1. 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.

2.2. 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 24 h (**3**). In all cases, ethynylferrocene, 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 24 h. 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.

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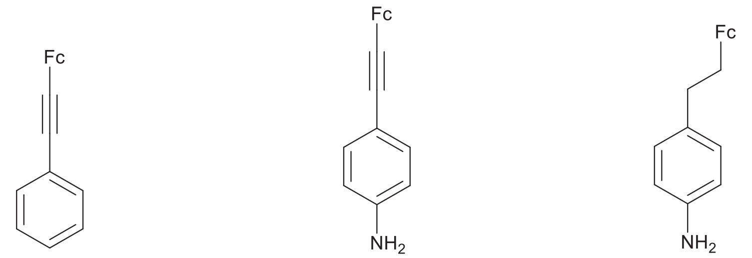

Phenylethynylferrocene (**1**) 4-(ferrocenylethynyl)aniline (**2**) 4-(2-ferrocenylethyl)aniline (**3**)

Scheme 1. The ferrocenyl compounds studied.

2.3. 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 Kα monochromatic beam working at 1486.6 eV. All

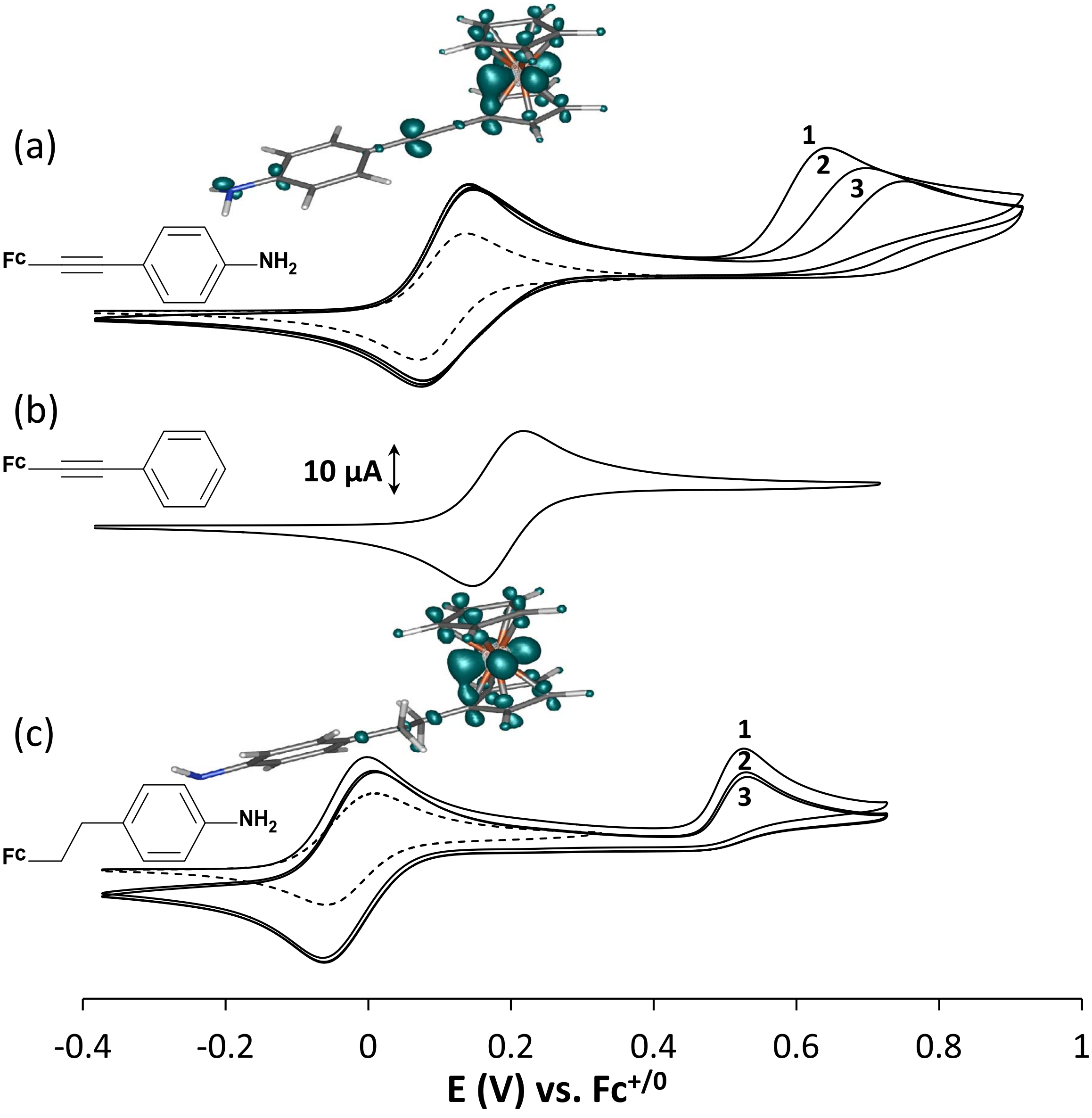

Fig. 1. CVs recorded on a GC electrode at 100 mV/s (solid lines) and 50 mV/s (dotted lines) in 1 mM acetonitrile solutions of 4-(ferrocenylethynyl)aniline (a), phenylethynylferrocene (b) and 4-(2-ferrocenylethyl)aniline (c). Computational modelling of the charge distribution following the first one-electron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