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Amplification upon polymerization of the electrochemical anion sensing properties of an amidoferrocene monoreceptor molecule

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Abstract

Oxidative electropolymerization of pyrrole-substituted monoamidoferrocene **1** yields redox polymer films showing marked electrochemical sensing properties towards $H_2PO_4^-$ and ATP^{2-} anions in organic electrolytes, as demonstrated by differential pulse voltammetry experiments. This behavior contrasts with the poor sensing properties of monomer **1**. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Ferrocene; Functionalized polypyrrole; Electrochemical sensing; Dihydrogenphosphate; ATP

1. Introduction

Chemically sensitive redox materials designed to detect a specific molecule or class of molecules have potential as chemosensors, especially when affixed to electrodes [1]. Much work has been devoted to conductimetric and potentiometric sensing devices based on conducting polymers films functionalized with receptors or complexing units [1–3]. In these systems, the conducting polymer matrice is the active component transducing responses to analytes. An alternative approach is to produce redox responsive macromolecular assemblies from molecular receptors incorporating redox-active centers.

A number of reports have shown that metallocene-containing hosts are useful in anionic electrochemical recognition [4]. Receptors containing neutral ferrocenyl units exhibit interesting anion recognition effects, because a strong electrostatic interaction is switched on by oxidation of ferrocene to ferrocenium. Ferrocenyl hosts can thus coordinate and electrochemically recognize anionic guest species via the cooperative binding forces of electrostatic interactions and other specific interactions, especially hydrogen-bonding with appended thiourea [5], guanidinium [5], amide [6,7], pyrrole [8] or protonated polyamines [9] H-donor groups. Shape selectivity and topological effects also influence both anion-receptor interaction and recognition ability in ferrocenyl hosts based on calixarene [10] and cyclotriveratrylene [11] platforms, in dendrimers [12,13] and in colloids [14,15].

To date, only a few examples of redox-active materials synthesized from ferrocenyl receptors have appeared [13–17]. The simple, well-behaved and robust redox activity of the ferrocene group confers to such materials a high potential for the electrochemical sensing of analytes. The electrochemical sensing of oxo-anions in organic media has been achieved using electrodeposited films of ferrocenyl dendrimers [13], gold colloids functionalized with amidoferrocenyl thiols [14] or dendrons with amidoferrocenyl termini [15], and poly(pyrrole-ferrocenylalkylammonium) films [16]. We herein report that a macromolecular material synthesized by electropolymerization of the pyrrole-containing monoamidoferrocenyl derivative **1** presents an enhanced electrochemical response to dihydrogenphosphate and ATP anions in organic electrolytes, as compared with that observed with the amidoferrocene monoreceptor system.

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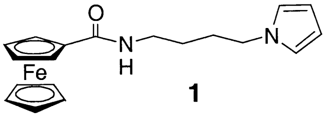

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2. Results and discussion

The cyclic voltammetry (CV) curves for **1** exhibit the regular wave corresponding to the reversible ferrocene/ferrocenium (Fc/Fc$^+$) redox couple ($E_{1/2}=0.25$ V; $\Delta E_p=70$ mV at $v=0.1$ V s^{-1}) in acetonitrile containing 10^{-1} M tetra-*n*-butylammonium perchlorate (TPAP). At higher potentials, an irreversible anodic peak is seen around 1 V corresponding to the irreversible oxidation of the appended pyrrole group. The growth of poly**1** films onto the electrode surface was readily accomplished either by repeated scans over the −0.2 to 0.9 V potential range, or by controlled potential electrolysis at 0.95 V in CH_3CN solution containing 10^{-3} M **1**. After transfer in monomer-free electrolyte, the CV curves of the resulting modified electrodes display the electrochemical response of the immobilized **1** at $E_{1/2}=0.26$ V ($\Delta E_p=10$ mV, at $v=50$ mV s^{-1}). The apparent surface concentration of amidoferrocene species, Γ, in poly**1** films was determined from the integration of the current under the Fc/Fc$^+$ oxidation peak. Typically, coatings containing around 10^{-9} mol cm^{-2} of amidoferrocene units were obtained by using a polymerization charge of 0.33 mC.

The sensing properties of poly**1** towards various oxoanions have been examined from differential pulse voltammetry (DPV) experiments (Table 1). Pt/poly**1** modified electrodes ($\Gamma=10^{-9}$ mol cm^{-2}) are characterized by a well-behaved DPV peak at $E_p=0.26$ V (Fig. 1A, curve 1). Addition of increasing amounts of $H_2PO_4^-$ anions to the CH_3CN solution leads to the decrease of the intensity of the initial wave. The growth of a new peak is then observed at a less positive potential, until the initial wave has disappeared after the addition of at least 10^{-3} M $H_2PO_4^-$ (Fig. 1A, curve 5). The potential of the new signal is progressively shifted from 0.14 V at low $H_2PO_4^-$ concentration (ca. 10^{-5} M), down to a constant value of 0.04 V at higher concentration (ca. 5×10^{-4} M) of dihydrogenphosphate. This signal appears as a shoulder at low $H_2PO_4^-$ concentration (Fig. 1A, curve 2) and adopts the feature of a clear DPV peak at higher concentration (Fig. 1A, curve 3). The binding of anions effectively stabilizes the positive charge of the oxidized film, causing the Fc/Fc$^+$ redox couple to shift to less positive potentials.

The intensity of DPV peaks is somewhat depressed in the presence of $H_2PO_4^-$ ions, even at low concentration (Fig. 1A, curves 1–5). The loss of electroactivity could be linked to ion-pairing between dihydrogenphosphate and ferrocenium in the oxidized polymer film. As already noticed for other redox polymer films [16,18], charge propagation and, thus, electroactivity of poly**1** appears dominated by counter-ion diffusivity and ion-trapping effects.

Analysis of the intensity of the new DPV peak allows to draw an amperometric titration curve (Fig. 1B), which presents low and high limits of detection of 10^{-5} and 2×10^{-4} M in $H_2PO_4^-$, respectively. It can be assumed that the factors involved in the electrochemical sensing properties of poly**1** towards the dihydrogenphosphate anion are the H-bonding interaction with amido groups and the enforced electrostatic interaction in the oxidized (ferrocenium) film [4]. As expected, polarity of the solvent plays a central role in the electrochemical recognition ability of poly**1** towards $H_2PO_4^-$. The potential shift is higher in CH_2Cl_2 ($\Delta E_p=-0.26$ V) than in CH_3CN ($\Delta E_p=-0.22$ V), in agreement with increased electrostatic interactions in less polar solvent. It is remarkable that the sensing behavior of poly**1** is much important than that of monomer **1**. Addition of increasing amounts of $H_2PO_4^-$ to a solution of 1 mM **1** in CH_3CN only produced a progressive, weak negative shift of the initial Fc/Fc$^+$ CV wave ($\Delta E_p=-0.08$ V with six equivalents of anion added; Fig. 2).

The CV response of **1** in the presence of an excess of $H_2PO_4^-$ is characterized by a large increase in the anodic peak current along with a decrease in the reversibility of the Fc/Fc$^+$ wave (Fig. 2, curve 4). This behavior is characteristic of an EC mechanism with product adsorption and indicates the formation of strong **1**$^+$–

Table 1
Differential pulse voltammetry data for poly**1** ($\Gamma=10^{-9}$ mol cm^{-2}) in the presence of 10^{-3} M $H_2PO_4^-$, ATP^{2-}, HSO_4^- and NO_3^-, in CH_3CN and CH_2Cl_2 containing 10^{-1} M TBAP

Solvent	Free poly**1**, E_p [a] (V)	Poly**1**+$H_2PO_4^-$, ΔE_p [b] (mV)	Poly**1**+ATP^{2-}, ΔE_p [b] (mV)	Poly**1**+HSO_4^-, ΔE_p [b] (mV)	Poly**1**+NO_3^-, ΔE_p [b] (mV)
CH_3CN	0.26	−220	−180	−30	[c]
CH_2Cl_2	0.34	−260	−240	−90	[c]

[a] Versus Ag/Ag$^+$ 10^{-2} M+TBAP 10^{-1} M+CH_3CN; scan rate 10 mV s^{-1}; pulse height 25 mV; step time 0.2 s.

[b] $\Delta E_p=E_p([A^-]=10^{-3}\text{ M})-E_p([A^-]=0)$.

[c] No variation of the electrochemical response.

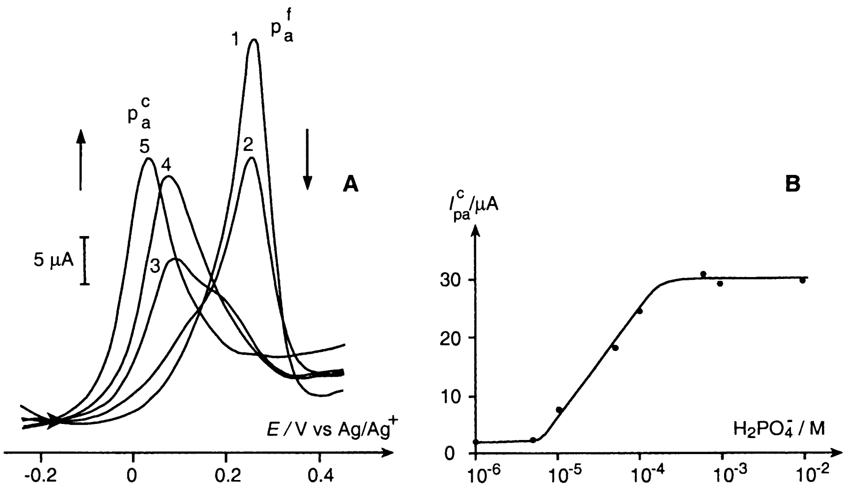

Fig. 1. (A) DPV curves recorded at a poly**1**/Pt disc electrode (5 mm in diameter, $\Gamma = 10^{-9}$ mol cm^{-2}) in $CH_3CN + 10^{-1}$ M TBAP; $H_2PO_4^- = 0$ (1), 10^{-5} M (2), 5×10^{-5} M (3), 10^{-4} M (4), 10^{-3} M (5); sweep rate 0.01 V s^{-1}; pulse height 25 mV; step time 0.2 s. (B) Amperometric titration curve of dihydrogenphosphate in CH_3CN; $\Gamma = 10^{-9}$ mol cm^{-2}.

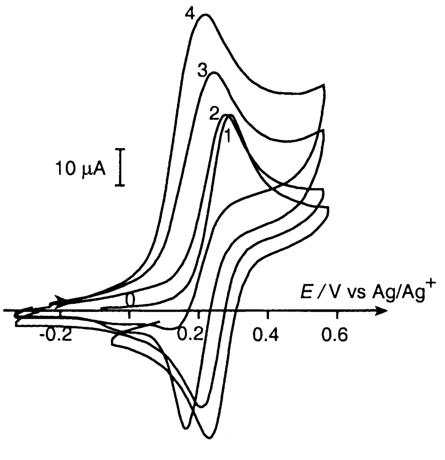

Fig. 2. CV curves in $CH_3CN + 10^{-1}$ M TBAP at Pt disc electrode (5 mm in diameter) of 10^{-3} M **1**; $H_2PO_4^-/$**1** = 0 (1), 0.4 (2), 2.4 (3), 6 (4); sweep rate 0.1 V s^{-1}.

$H_2PO_4^-$ ion pairs that remain strongly adsorbed onto the electrode surface. The interaction between dihydrogenphosphate and monomer **1** in its reduced state surely takes place via H-bonding of the anion to amide proton and appeared very weak ($K = 14$ M^{-1} in CD_3CN; measured by standard ^{1}H-NMR titration [11], monitoring the shift of the H amide proton resonance on addition of increasing amounts of anion; $\Delta\delta_{max} = 0.86$ ppm).

It is probable that the very high concentration of amidoferrocene moieties in poly**1**[1] creates a favorable topological and concentration effect comparable to that obtained in dendrimers [12,13] and dendronized colloids [14,15]. Multiple hydrogen bonding between anions and amide groups in the film could be involved in the recognition properties of poly**1**. Moreover, the ferrocenium groups in the oxidized film are in close proximity, which is responsible of very strong electrostatic interactions with the trapped anions. Poly**1** can be thus seen as a macromolecular receptor material that produces larger electrochemical sensing properties than those afforded by monomer units.

Interestingly, poly**1** presents a similar behavior in the presence of ATP^{2-} anions, i.e. the rise of a new DPV peak at a less positive potential at the expense of the initial peak of the free polymer film. The potential shift is larger in CH_2Cl_2 ($\Delta E_p = -240$ mV) than in CH_3CN ($\Delta E_p = -180$ mV) (Table 1). In contrast, the addition of increasing amounts of HSO_4^- leads only to a progressive, small shift of the potential of the initial Fc/Fc$^+$

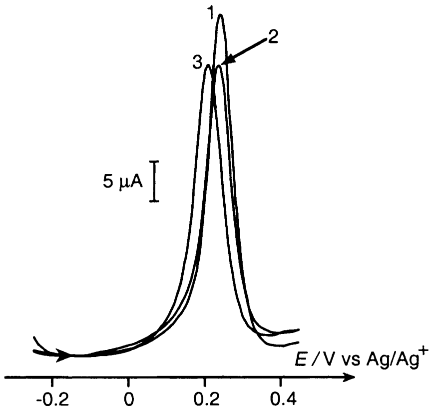

Fig. 3. DPV curves in $CH_3CN + 10^{-1}$ M TBAP recorded at a poly**1**/Pt disc electrode (5 mm in diameter; $\Gamma = 10^{-9}$ mol cm^{-2}); $HSO_4^- = 0$ (1), 10^{-5} M (2), 10^{-3} M (3); sweep rate 0.01 V s^{-1}; pulse height 25 mV; step time 0.2 s.

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[1] It is well-established that the concentration of active species in redox polymer films lies in the 1.5-3 M range; see for example: P. Burgmayer, R. W. Murray, *J. Electroanal. Chem*. 135 (1982) 335; R. H. Schmehl, R. W. Murray, *J. Electroanal. Chem*. 152 (1983) 97.

wave (Fig. 3 and Table 1). In addition, no significant change was observed on the DPV curves of poly**1** even in the presence of excess NO_3^- ions.

3. Conclusion

The electropolymerization of a simple monoamidoferrocene derivative containing a pyrrole group is a straightforward way to synthesize redox polymer films that can sense $H_2PO_4^-$, ATP^{2-} and HSO_4^-, with excellent selectivity for the former anions. The polymer film presents enhanced electrochemical sensing properties as compared with the amidoferrocene monomer. It can be reasonably assumed that the high local concentration of amido and ferrocene/ferrocenium groups reached in the polymer is responsible of this improved sensing behavior towards oxo-anions. The poly(amidoferrocene) can be thus seen a macromolecular anion redox-receptor.

4. Experimental

Monomer **1** was synthesized by reaction of 0.6 mmol of 1-chlorocarbonyl ferrocene [19] and 0.65 mmol of 1-(4-aminobutyl)pyrrole [20] in 15 ml of dried CH_2Cl_2 containing a stoichiometric amount of Et_3N. The mixture was stirred overnight at room temperature (r.t.) under an Argon atmosphere. Water was then added and the mixture was extracted with CH_2Cl_2. The organic phase was washed with H_2O, dried over $MgSO_4$ and the solvent was removed in vacuum. Monomer **1** was purified by chromatography on silica gel eluted with CH_2Cl_2–MeOH, (99:1, v/v) and obtained as a yellow solid; yield 75% (based on 1-chlorocarbonylferrocene). M.p. 105 °C. Elemental analysis: Found: C, 65.21; H, 6.57; N, 7.81; $C_{19}H_{22}N_2FeO$ requires: C, 65.16; H, 6.33; N, 8.00%. FABMS, *m/z* (positive mode): 350 $[M^+]$. ^{1}H-NMR ($CDCl_3$): 1.53 (q, CH, $C\boldsymbol{H}_2{-}CH_2$–pyrrole), 1.83 (q, 2H, NH–$CH_2{-}C\boldsymbol{H}_2$), 3.36 (q, 2H, $C\boldsymbol{H}_2$–pyrrole), 3.92 (t, 2H, NH–$C\boldsymbol{H}_2$), 4. 16 (s, 5H, $\boldsymbol{H}$-Cp), 4.31(s, 2H, $\boldsymbol{H}_\beta$-Cp), 4.61 (s, 2H, $\boldsymbol{H}_\alpha$-Cp), 5.62 (s, 1H, N$\boldsymbol{H}$–CO), 6.14 (t, 2H, $\boldsymbol{H}_\beta$-pyrrole), 6.65 (t, 2H, $\boldsymbol{H}_\alpha$-pyrrole). ^{13}C-NMR ($CDCl_3$): 27.29 ($CH_2{-}\boldsymbol{C}H_2{-}CH_2$–pyrrole), 28.82 ($CH_2{-}\boldsymbol{C}H_2{-}CH_2$–NH), 38.89 ($\boldsymbol{C}H_2$–pyrrole), 49.08 ($\boldsymbol{C}H_2$–NH), 67.94, 69.64, 70.37, 76.07 (Cp), 108.03, 120.17 (pyrrole), 170.20 ($\boldsymbol{C}$O–NH).

Electrochemical experiments were conducted in a three-electrode cell at room temperature. The working electrode was a platinum disc (5 mm in diameter) polished with 1 μm diamond paste. The reference electrode used was the Ag/10^{-2} M Ag^+ (as $AgNO_3$) in CH_3CN+10^{-1} M tetra-*n*-butylammonium perchlorate (TBAP) system. The potential of the regular ferrocene/ferrocenium (Fc/Fc^+) redox couple is 0.07 V under our experimented conditions in acetonitrile. Differential pulse voltammetry curves were recorded at a 10 mV s^{-1} scan rate with a pulse height of 25 mV and a step time of 0.2 s.

Methanol (SDS, 99%, purex analytical grade) and MeCN (Rathburn, HPLC grade S) were used as received. Dichloromethane was dried over neutral alumina oxide (activity I) for at least 4 days before use. TBAP (Fluka) was dried under vacuum at 80 °C for 3 days. Tetraethylammonium nitrate, tetrabutylammonium hydrogensulphate and dihydrogenphosphate were of the highest purity commercially available and were used without purification. The di(tetra-*n*-butylammonium) salt of adenosine-5′-triphosphate (ATP^{2-}) was obtained from its corresponding disodium salt by ion exchange on Amberlite IRC 50 in $(n\text{-}Bu)_4N^+$ form.

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