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ChemComm
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Redox sensing of anions in pure aqueous environment by ferrocene-containing 4,4′-bipyridinium-based receptors and polymer films†

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Received (in Cambridge, UK) 7th November 2003, Accepted 16th December 2003
First published as an Advance Article on the web 22nd January 2004

Selective voltammetric sensing of ATP^{2-} anions in water was achieved using ferrocene-viologen based redox active receptors and related polymer films.

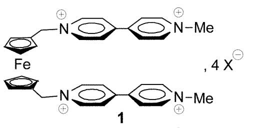
The electrochemical recognition of anionic species by artificial molecular hosts is currently an area of intense interest.[1,2] Receptors capable of operating in competitive solvents, such as water, are obviously important given the prevalence of anions in biological systems and in the environment. However, redox hosts that have the ability to bind and sense anionic species in purely aqueous solvents are rare.[2]

Here we report the electrochemical sensing of anions in water using ferrocene-containing viologen (4,4′-bipyridinium) receptors (**1**, **2**) and electrode material (*poly*-**3**). It is well-known that viologen[3] and, better still, macrocyclic bisviologen[4] derivatives form strong charge transfer complexes with a variety of π-donor neutral or anionic molecules, including biologically relevant species. Furthermore, the cyclobis(paraquat-*p*-phenylene) host **4** can detect electron-rich guests through potential shifts of the viologen-localized redox couples.[4–6]

In receptors **1–3**, the ferrocene units can be considered as dual-action molecular tools: (i) a guest can be detected and monitored through a change in the electrochemical behaviour of the metallocene moieties, at easily accessible potentials and under aerobic conditions; and (ii) the extra positive charges switched-on by oxidation of the ferrocene centers increase the anion binding properties of the receptors.

Compounds **1**[7] and **2** were synthesized by quaternization of 4,4′-bipyridine with 1,1′-di(chloromethyl)ferrocene, followed by reaction with iodomethane or 1,1′-di(chloromethyl)ferrocene under conditions of high dilution, respectively. Monomer **3** was obtained by reaction of 4,4′-bipyridine with chloromethylferrocene, followed by action of bromopropylpyrrole. The **1**, **2** and **3** compounds were isolated as their PF_6^- and NO_3^- salts and characterized by ^1H and ^{13}C NMR spectroscopy, elemental analysis and mass spectrometry.[8]

Results of the cyclic voltammetry (CV) investigations performed on **1** and **2** in aqueous solution are summarized in Table 1. Both viologen-localized one-electron reduction waves ($V^{2/\cdot+}$ and $V^{\cdot+/0}$ systems) are severely distorted, due to the strong adsorption of the reduced forms of the receptors on the electrode surface (Fig. 1). In contrast, oxidation of the ferrocene centers ($Fc^{0/+}$) is characterized by a well-behaved CV wave.



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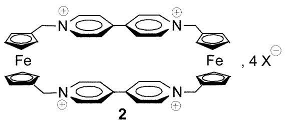

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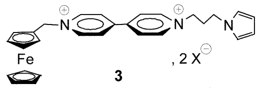

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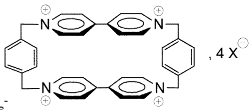

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$X^{\ominus} = NO_3^-$ or PF_6^-

The sensing properties of **1** and **2** towards various halides and oxoanions were examined from CV and differential pulse voltammetry (DPV) experiments (Table 2).

Due to strong adsorption phenomena, changes in the viologen-centered reduction waves could not be investigated, but the anionic recognition properties of **1** and **2** were easily assessed from changes in the ferrocene-based electroactivity. No significant modifications were observed with $H_2PO_4^-$, SO_4^{2-}, HPO_4^{2-}, CF_3COO^-, F^- or Cl^-. A small but measurable shift (−10 mV) of the $Fc^{0/+}$ system was observed in the presence of HSO_4^- (for **1**), $PhPO_4^{2-}$ (for **2**), $S_2O_4^{2-}$ (for **1** and **2**) and ATP^{2-} (for **1**). In contrast, the ATP^{2-}

Table 1 Electrochemical data for **1**, **2** and *poly*-**3** in H_2O containing 0.05 M KNO_3[a]

Compound	$E_{1/2}$ [ΔE_p][b] $Fc^{0/+}$/mV	$E_{1/2}$ [ΔE_p][b] $V^{2+/\cdot+}$/mV	$E_{1/2}$ [ΔE_p][b] $V^{\cdot+/0}$/mV
1	640 [80]	−550 [90]	−970 [220]
2	640 [80]	−380 [70]	−950 [260]
Poly-**3**[c]	475 [5]	−435 [90]	−875 [170]

[a] Reference electrode SCE, 3 mm diameter carbon disk electrode, scan rate 100 mV s^{-1}; [b] $E_{1/2} = (E_{pa} + E_{pc})/2$; $\Delta E_p = E_{pa} - E_{pc}$; [c] $\Gamma = 10^{-9}$ mol cm^{-2}.

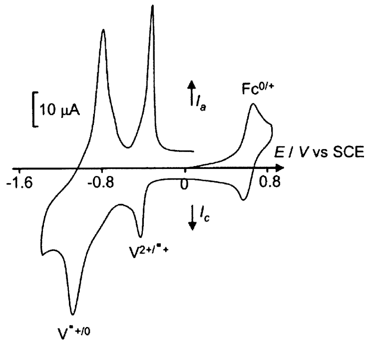

Fig. 1 Cyclic voltammogram of a solution of **2** (10^{-3} M) in H_2O + 0.05 M KNO_3 (scan rate 100 mV s^{-1}, 3 mm diameter carbon disk).

Table 2 DPV data for **1**, **2** and *poly*-**3** in the presence of ATP^{2-}, HSO_4^-, $PhPO_4^{2-}$ and $S_2O_4^{2-}$ in H_2O containing 0.05 M KNO_3.[ab]

	Free receptor E_{pa}/mV	HSO_4^- ΔE_p/mV	$S_2O_4^{2-}$ ΔE_p/mV	$PhPO_4^{2-}$ ΔE_p/mV	ATP^{2-} ΔE_p/mV
1[c]	630	−10	−10	0	−10
2[c]	630	0	−10	−10	−25
Poly-**3**[d]	460	−20	−10	0	−35

[a] Reference electrode SCE, scan rate 20 mV s^{-1}. [b] $\Delta E_p = E_{pa}$ ($[A^-] \neq 0$) − E_{pa} ($[A^-] = 0$). [c] $[A^-]$ = two-molar equivalents. [d] $\Gamma = 10^{-9}$ mol cm^{-2}, $[A^-] = 10^{-3}$ M.

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† Electronic supplementary information (ESI) available: electrochemical behaviour and characterization of monomer **3** and *poly*-**3**. See http://www.rsc.org/suppdata/cc/b3/b314236a/

DOI: 10.1039/b314236a

anion is clearly and selectively recognized by receptor **2**. A progressive negative potential shift of the $Fc^{0/+}$ wave was obtained upon addition of increasing amounts of this anion to a solution of **2**. The shift reached −25 mV in the presence of two-molar equivalents of ATP^{2-}. This selective sensing is believed to be due to specific electrostatic interactions between the ATP^{2-} anion and **2** in its reduced form, which are re-inforced in the oxidized hexacationic form of the receptor ("switch-on process"). Additional charge-transfer interactions between the viologen moieties and ATP^{2-}, which contains the electron-rich adenosine group, can also be invoked[9] to explain the observed selectivity. This assumption is corroborated by a UV-visible spectroscopic study, which revealed an increase of the absorbance of ferrocene at 452 nm, upon addition of ATP^{2-} to a solution of **2**. Moreover, in accordance with the results obtained with other viologen receptors,[5,6] comparison of the sensing properties of **1** and **2** suggests that the preorganization of the receptor **2** has a significant role in the guest recognition.

Poly-**3** films were deposited onto electrode surfaces by oxidative electropolymerization (0.9 V *vs.* Ag/Ag^+ 10^{-2} M in CH_3CN + TBAP 0.1 M) of the pyrrole fragment, in millimolar solutions of **3** in CH_3CN + TBAP 0.1 M.[10] After transfer of the resulting modified electrode in monomer-free CH_3CN electrolyte, the CV curve displayed the stable and reversible electrochemical response of the immobilized **3** (Fig. 2A), characterized by the oxidation of the metallocene group at +230 mV and the two successive viologen-based reductions at −655 and −1160 mV ($\Delta E_p \approx 0$ mV at $v = 100$ mV s^{-1}).

The electrochemical properties of the modified electrodes in H_2O + 0.05 M KNO_3 were then examined from CV (Fig. 2B and Table 1) and DPV (Fig. 3A) experiments. No changes were observed in the presence of $H_2PO_4^-$, $PhPO_4^{2-}$ or halide anions. On the contrary, the ferrocene signal shifted negatively upon addition of HSO_4^-, $S_2O_4^{2-}$ and ATP^{2-} (Fig. 2B and Table 2). As in the case of receptor **2** the largest shift of the $Fc^{0/+}$ signal was obtained in the presence of ATP^{2-} ($\Delta E_{max} = -35$ mV). Quantitative analysis of the sensing properties of *poly*-**3** films in the presence of ATP^{2-} was achieved from DPV experiments. The ferrocene oxidation peak is progressively shifted from $E_p = 460$ mV at low ATP^{2-} concentration (10^{-5} M) down to a constant value of $E_p = 425$ mV at higher ATP^{2-} concentration (10^{-3} M), and a potentiometric titration curve could be drawn (Fig. 3B). It can be assumed that the high concentration of complexing sites in close proximity on the electrode surface obtained by electropolymerization of **3** creates a "macromolecular effect", allowing the efficient detection of ATP^{2-} in water. A similar amplification effect has already been observed in the course of the electrochemical detection of anions in organic solvents with polyamidoferrocene[11] and polyamidocobaltocenium[12] films, or gold colloids functionalized with amidoferrocenyl dendrons.[13]

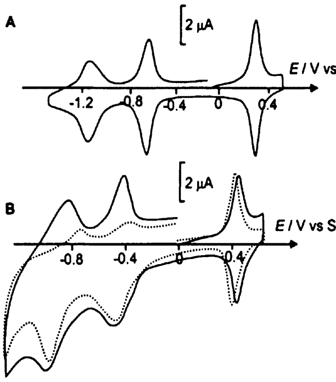

Fig. 2 Cyclic voltammograms recorded at a *poly*-**3**/carbon disk electrode (3 mm in diameter, $v = 100$ mV s^{-1}, $\Gamma = 10^{-9}$ mol cm^{-2}) (**A**) in CH_3CN + 10^{-1} M TBAP and (**B**) in H_2O + 0.05 M KNO_3; $[ATP^{2-}] = 0$ M (full line) and 10^{-3} M (dotted line).

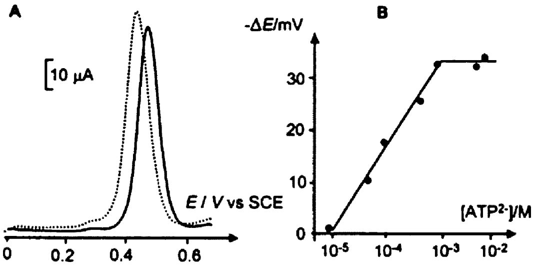

Fig. 3 (A) DPV curves recorded at a *poly*-**3**/carbon disk electrode (3 mm in diameter, $\Gamma = 10^{-9}$ mol cm^{-2}) in H_2O + 0.05 M KNO_3, without ATP^{2-} (full line) and with 10^{-3} M ATP^{2-} (dotted line), scan rate 20 mV s^{-1}. (B) corresponding potentiometric titration curve.

It can be concluded that the ferrocene group acts an efficient, simple and air-stable redox probe which allows, when closely associated with viologen moieties, electrochemical sensing of anionic species in water. Besides strong electrostatic interactions between the positively charged bipyridinium fragments and the anionic guests, reinforced as ferrocene is oxidized to ferricinium, the observed selectivity towards ATP^{2-} most probably arises from a specific charge transfer process between this π-donor anion and the electron acceptor viologen groups. These results especially emphasize the importance of conjugating a number of different host–guest interactions in order to achieve electrochemical detection of anionic species in water.

Moreover, the electrochemical recognition properties observed in homogeneous phase have been significantly enhanced through the use of a poly(ferrocene-viologen) film electrode. This redox-active material acts as a polymeric receptor whose physico-chemical and topological features generate a "macromolecular effect" responsible for the sensing improvement. This strategy can be considered as an effective way towards effective anion sensing devices in competitive media.

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8 **1**: FAB-MS *m/z*: 740 $[M - 3NO_3]^+$; ^1H NMR (D_2O) δ: 4.43 (s, 6H), 4.55 (d, 4H), 4.68 (d, 4H), 5.76 (s, 4H), 8.42 (d, 8H), 8.99 (m, 8H). ^{13}C NMR (D_2O) δ: 51.11, 63.72, 73.97, 74.70, 81.98, 129.41, 129.59, 147.36, 149.06, 152.51, 152.94; **2**: ES-MS: *m/z* 1171 $[M - 3PF_6^-]^+$; ^1H NMR (D_2O) δ: 4.51 (d, 8H), 4.66 (d, 8H), 5.65 (s, 8H), 8.28 (d, 8H), 8.85 (d, 8H). ^{13}C NMR (D_2O) δ: 63.78, 73.91, 74.70, 81.92, 128.74, 147.30, 189.48; **3**: FAB-MS: *m/z* 608 $[M - PF_6]^+$; ^1H NMR (CD_3CN) δ: 2.84 (q, 2H), 4.21 (t, 2H), 4.31 (s, 5H) 4.40 (d, 2H), 4.68 (d, 2H), 4.96 (d, 2H), 6.00 (t, 2H), 6.05 (s, 2H, $-CH_2$-Cp), 6.68 (t, 2H) 8.72 (t, 4H), 9.26 (d, 2H), 9.36 (d, 2H). Anal. Calcd. For $C_{28}H_{29}N_3FeP_2F_{12}$: C, 44.53; H, 3.87; N, 5.56. Found: C, 44.64; H, 3.88; N, 5.57%.
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