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An electrochemical study in acetonitrile of macrocyclic or open-chain ferrocene-containing oxa-aza or polyaza receptors in the presence of protons, metal cations and anions

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Abstract

Electrochemical studies on redox-active macrocyclic and open-chain ferrocene-containing oxa-aza or polyaza receptors were carried out in acetonitrile in the presence of protons, cations and anions. Electrochemical studies in the presence of H^+, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+} and Pb^{2+} with L^4 (1,15-diferrocenyl-2,5,8,11,14-pentaazapentadecane) and L^5 (1,4,7,10,13-penta(ferrocenylmethyl)-1,4,7,10,13-pentaazacyclopentadecane) resulted in shift of the ferrocene oxidation wave to more positive potentials with maximum shifts for L^4 in the presence of Zn^{2+} and for L^5 in the presence of Ni^{2+}, Cu^{2+} and Hg^{2+} of 80 mV. In contrast, L^1 (10-ferrocenylmethyl-1,4,7-trioxa-10-azacyclododecane), L^2 (1,8-bis[bis(ferrocenylmethylamino)]-3,6-dioxaoctane) and L^3 7,13-bis(ferrocenylmethyl)-1,4,10-trioxa-7,13-diazacyclopentadecane) show a two-wave behaviour for H^+, Pb^{2+} and Hg^{2+} allowing the amperometric titration of these metal cations. The maximum oxidation peak shift of 290 mV was found for L^1 in the presence of Hg^{2+}. Electrochemical behaviour with anions ($H_2PO_4^-$, HSO_4^-, Br^- and Cl^-) in acetonitrile show that L^2 and L^6 (1,8-bis(ferrocenylmethylamino)-3,6-dioxaoctane) electrochemically sense $H_2PO_4^-$. For L^2 a cathodic shift of the oxidation peak of 190 mV and a shift of 346 mV to lower potential for the reduction peak was found. L^6 shows a similar behaviour. This electrochemical sense of $H_2PO_4^-$ was observed even in the presence of excess of other anions (HSO_4^- or Cl^-) in anion competition experiments. © 2001 Published by Elsevier Science B.V.

Keywords: Electrochemistry; Anion sensing; Cation sensing; Ferrocene

1. Introduction

The possibility of producing new materials of relevance to the field of molecular sensors has led in recent years to considerable interest in the synthesis of redox-active molecules that contain a redox centre in close proximity to a cation or anion binding site [1,2]. Bearing in mind that the binding process in these systems may lead to a shift of the oxidation potential of the redox-active groups, they may be considered as potentially new electrochemical cation- or anion-sensing receptors [3]. The magnitude of the shift in the redox potential produced by guest binding is a factor of primary importance for the development of potential prototypes of amperometric devices [4]. In particular, it has been suggested that an added degree of recognition is conferred by appearance of a new set of redox waves (two-wave behaviour) associated with the oxidation of the ferrocenyl subunits in the host-guest complex, compared with a single gradual shift in the potential of the original ferrocene redox couple [5].

On the other hand, the molecular recognition of anionic guest species of biochemical, medical and environmental importance is an area of intense current research activity [6–8]. The natural extension of such work is to develop sensors for anions, molecules which will exhibit a measurable physical change upon anion binding [8–11]. The interaction between the ferrocene-functionalised receptors and a certain guest can be electrostatic or via formation of hydrogen bonds [12]. Additionally when the ferrocene groups are oxidised to ferricinium (Fc^+) an additional electrostatic interaction

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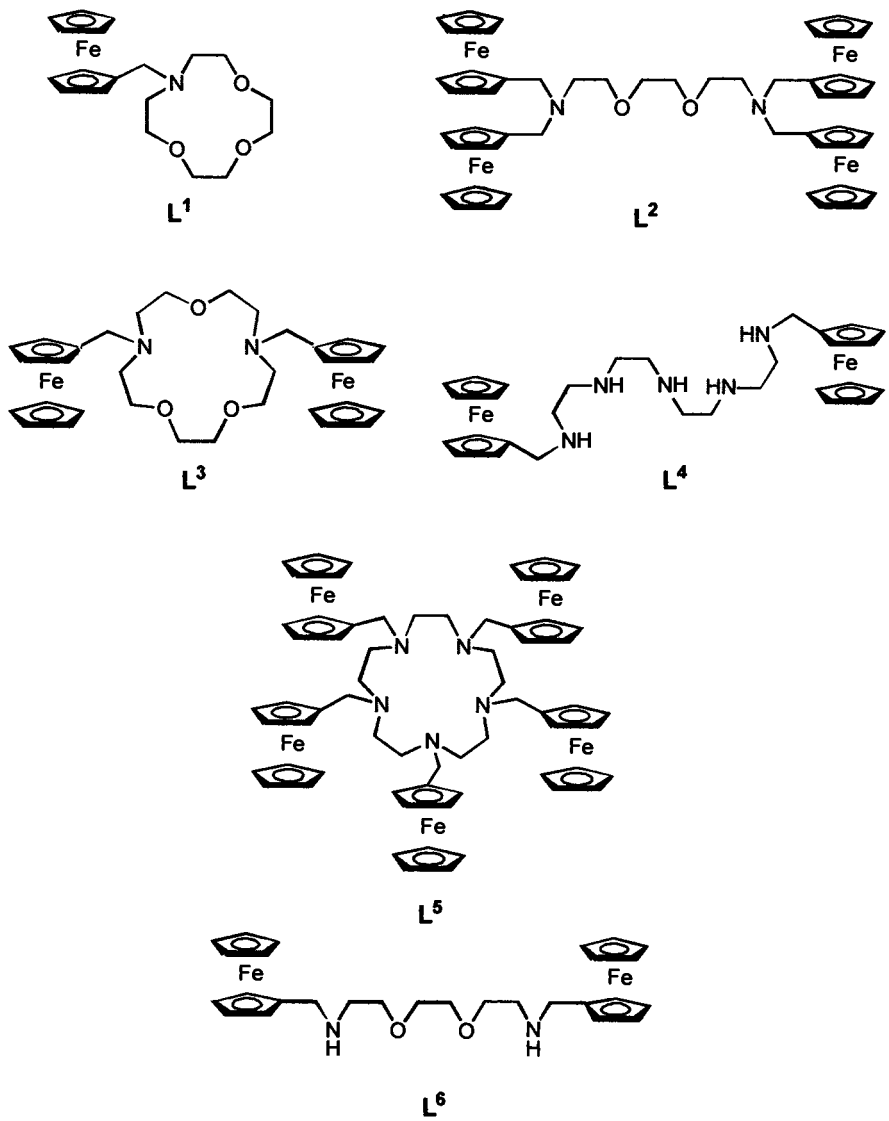
could be observed between the charged oxidised Fc^+ groups and the anion. We and others have recently prepared new redox-active ligands expressly designed to show electrochemical response towards a large variety of both anions and cations using polyaza or oxaaza crown derivatives [13–21]. We have published recently the synthesis of the receptor L^1 to L^5 and their electrochemical behaviour in water, dioxane:water or tetrahydrofuran:water mixtures [22–25]. From a practical point of view ferrocene functionalised receptors might be used in solution (probably in water) or can be incorporated into suitable amperometric devices. In the former case the use of molecules showing a large electrochemical response in an aqueous environment would be required. In contrast, the response of redox-active groups incorporated into a solid electrode would be quite different from that observed in water at least due to the lower relative permittivity in this medium. To further investigate the electrochemical behaviour of the ferrocene-functionalised receptors L^1–L^5 we report here the electrochemical response of these ligands in acetonitrile in the presence of H^+ and transition metals ions (Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+} and Pb^{2+}). Additionally, the study of the electrochemical response of L^1, L^2 and L^6 receptors in the presence of $H_2PO_4^-$, HSO_4^-, Cl^- and Br^- anions has also been carried out (Scheme 1).

2. Experimental

2.1. Solvents and reagents

Acetonitrile (CH_3CN) was pre-dried over molecular sieves (4–8 mesh) and then distilled under nitrogen from calcium hydride. The synthesis of receptors has



Scheme 1.

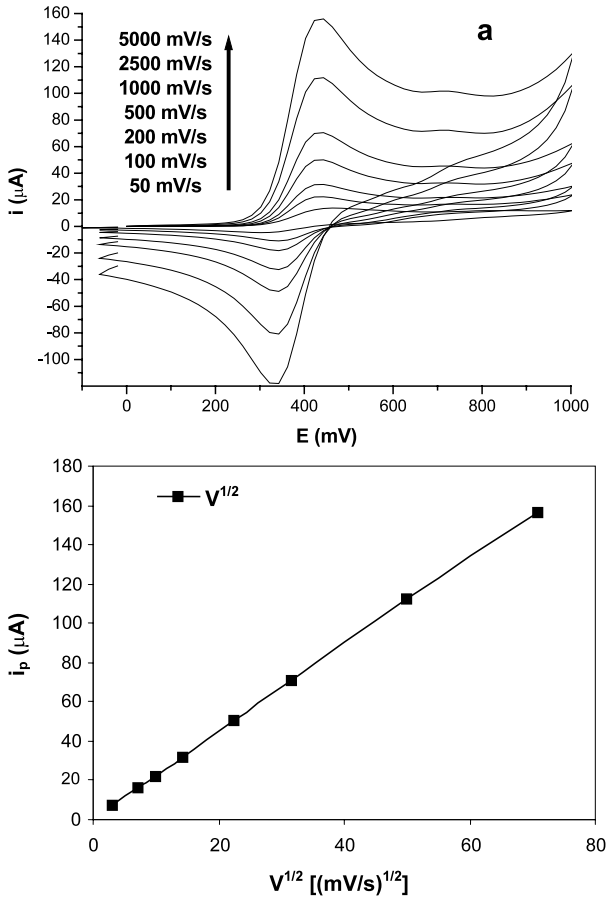


Fig. 1. (a) Cyclic voltammograms of L^1 in acetonitrile at different scan rates. (b) Linear relation between the anodic peak current and the square root of the scan rate.

been published elsewhere, see Ref. [22] for L^1, [23] for L^2 and L^3; Ref. [24] for L^4 and Ref. [25] for L^5. L^6 has been synthesised previously by Beer and Smith [26]. Metal cations Cu^{2+}, Ni^{2+}, Zn^{2+} and Cd^{2+} were used as their nitrate salts, and metal cations Pb^{2+} and Hg^{2+} were used as their perchlorate salts. Anions HSO_4^-, $H_2PO_4^-$, Cl^- and Br^- were used as their tetabutylammonium salts.

2.2. Physical measurements

Electrochemical data were carried out in dry acetonitrile (0.1 M tetrabutylammonium perchlorate as the electrolyte, 25 °C), with a programmable function generator Tacussel IMT-1, connected to a Tacussel PJT 120-1 potentiostat. The working electrode was platinum disk with a saturated calomel reference electrode separated from the test solution by a salt bridge containing the solvent/supporting electrolyte. The auxiliary electrode was a platinum wire. While cyclic voltammetry (CV) was employed in most cases to obtain electrochemical information, differential pulse voltammetry (DPV) was also used when additional accuracy and sensitivity were desired. The electrochemical response was recorded after progressively adding aliquots of stock solutions in acetonitrile containing substoichiometric or stoichiometric equivalents of metal ions or anions.

3. Results and discussion

3.1. Electrochemical behaviour of receptors in the presence of protons and metal cations

The main interest in the L^1–L^5 receptors is the incorporation of redox centres near binding sites. These redox-active groups can be affected by the presence of metal ions and transform chemical information at the molecular level (the presence or absence of a target guest) into a macroscopically observable signal (shift of the oxidation potential of the redox-active groups). We have already reported the electrochemical behaviour of the L^1–L^5 ligands in dioxane:water (70:30 v/v, 25 °C, 0.1 M KNO_3) in the presence of transition metals ions (Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+} and Pb^{2+}) [22–24]. Now we show the electrochemical properties of all these receptors in dry acetonitrile with Bu_4NClO_4 as the supporting electrolyte.

The L^1–L^5 receptors in acetonitrile show only one oxidation peak and the corresponding reduction peak is observed when the sweep is reversed. The oxidation/reduction couple appears to be reversible with a separation peak of ca. 100 mV (similar to that found for ferrocene under similar conditions) and with anodic and cathodic intensities ratios close to the unity. Plots of i_p versus $v^{1/2}$ (i_p = anodic peak intensity and v = scan rate) indicate that the oxidation is controlled by diffusion (see Fig. 1). Table 1 shown the voltammetric data for these receptors and their oxidation peak potential shift when full protonation is achieved. The oxidation potential of the L^1–L^5 ligands follows the order L^1 (450 mV) < L^3 (470) < L^2 = L^4 (500) < L^5 (505).

The behaviour of the receptors in the presence of *p*-toluenesulfonic acid was also investigated. The addition of acid produces protonation of the amines. This is a well-known effect that induces the receptor to become positively charged with the consequent increase of the oxidation potential of the ferrocenyl groups [27,28]. In fact, the redox potential of the ferrocene in compounds L^1–L^5 is anodically shifted upon successive addition of H^+. The largest increment was found for L^1 and L^3 with ΔE values of 220 and 200 mV, respectively, when fully protonated. These two receptors present a two-wave behaviour due the strong interaction between L^1 and L^3 with H^+ (see Fig. 2 for L^1). The addition of protons to L^2 ($2H^+$), L^4 ($5H^+$) and L^5 ($5H^+$) results in oxidation potential shifts of 135, 110 and 135 mV, respectively. The electrochemical shift in aqueous or

Table 1
Electrochemical data for L^1, L^2, L^3, L^4 and L^5 in acetonitrile in 0.1 M tetrabutylammonium perchlorate

	E_{pa} (V)	E_{pc} (V)	$E_{1/2}$ (V)	ΔE_p (mV)	i_{pa}/i_{pc}	ΔE (H^+) (mV)
L^1	450	340	395	110	1	220 ($1H^+$)
L^2	500	350	425	150	1	135 ($2H^+$)
L^3	470	380	425	90	1	200 ($2H^+$)
L^4	500	390	445	110	1	110 ($5H^+$)
L^5	505	410	457.5	95	1	135 ($5H^+$)

E_{pa} and E_{pc} are the oxidation and reduction wave potential on the CV; $E_{1/2} = (E_{pa} + E_{pc})/2$; $\Delta E_p = (E_{pa} - E_{pc})$; i_{pa} and i_{pc} are the oxidation and reduction wave currents. The potentials are listed versus SCE. ΔE (H^+) maximum anodic shift in E_{pa} after protonation.

aqueous–organic solutions for receptors L^1 to L^5 has recently been determined [22–24]. L^1 shows an increment of the oxidation potential of the ferrocenyl groups from basic to acidic pH of 200 mV in water, whereas receptors L^2, L^3, L^4 and L^5 gave electrochemical shifts from basic to acidic pH of 120, 160, 125 and 80 mV, respectively, in dioxane:water 70:30 v/v mixtures. The electrochemical shifts obtained in dioxane:water are slightly lower than those in acetonitrile. This is in line with the fact that the dielectric constant of acetonitrile ($\varepsilon = 37.5$) is lower than that of dioxane:water 70:30 v/v mixtures ($\varepsilon = 53.3$) [29]. The interaction between the positively charged ammonium groups and the ferrocenyl moieties have been reported to be mainly electrostatic and therefore it is expected to observe larger electrochemical shifts in solvents with a lower dielectric constants [3].

In a previous paper we presented an empirical equation based on a Coulomb charge model that allows calculation of the maximum oxidation potential shift of a certain receptor in its interaction with substrates (Eq. (1)) [30,31]:

$$\Delta E = \frac{1}{jn}\left[\frac{z_a z_b e^2 N_A}{4\pi\varepsilon_0\varepsilon F}\sum_j\sum_i\frac{1}{r_{ji}} + B\sum_j\sum_i\frac{1}{r_{ji}^2}\right] \quad (1)$$

In this equation z_a is the charge of the oxidised electro-active group, z_b is the charge of the substrate, j is the number of redox groups, and i the number of substrates at a certain r_{ji} distance from the redox centres. B is an empirical parameter that takes into account that the permittivity is not constant but a function of the distance (for acetonitrile B (mV $Å^{-2}$) = 2619). [30] Using equation 1 the oxidation potential shift predicted upon protonation of L^1 and L^5 receptors is 212 and 120 mV, respectively, values that are in good agreement with the electrochemical shifts observed experimentally (see above). Predicted values of the electrochemical shift for L^2, L^3 and L^4 from Eq. (1) are 74, 147 and 296. These values are quite different from those observed experimentally. However it should be noted that although equation 1 usually gives good agreement with experimental data, the calculations are based on the accurate knowledge of the ferrocene-ammonium distances. An inadequate estimation of these distances from molecular modelling programs will cause equation 1 to fail, as is the case for L^2, L^3 and L^4.

When the redox response of these receptors towards a range of metal cations was investigated two different types of electrochemical response were observed, corresponding to either protonation of the receptor (by the use of perchlorate or nitrate cation hydrated salts) or metal–ion coordination. [26] Protonation or coordination with cations can each produce a shift of the oxidation potential or a two-wave behaviour, depending on the magnitude of the electrochemical shift (ΔE). Thus, large values of ΔE usually result in a two-wave behaviour whereas low ΔE values produce a sequential shift of the oxidation potential. For instance, addition of metal ions to L^4 and L^5 results in a low electrochemical shift and therefore addition of sub-stoichiometric amounts of metal ions induce a sequential shift of the oxidation potential peak. In contrast quite large oxidation shifts were observed for L^1 and L^2 in the presence of certain metal ions and therefore addition of sub-stoichiometric amounts of these metals results a two-wave behaviour (see for instance Fig. 3).

For L^5, increments of ca. 80 mV in the presence of Cu^{2+}, Hg^{2+} and Ni^{2+} and of ca. 60 mV in the presence of Zn^{2+} and Cd^{2+} were observed. These results are similar to those obtained for the analogous

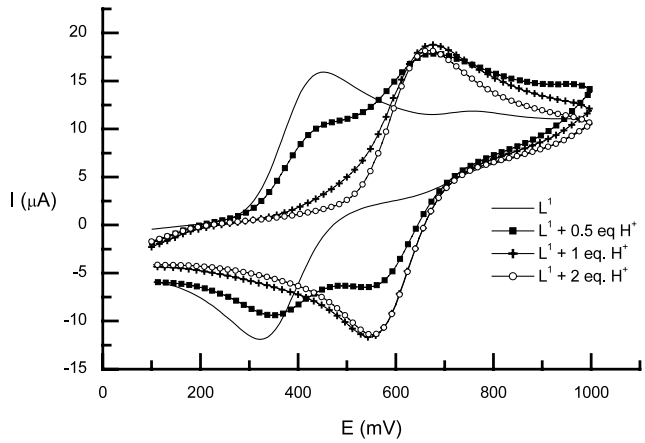


Fig. 2. Cyclic voltammograms of L^1 in presence of 1 equivalent of protons in dry acetonitrile, 0.1 M tetrabutylammonium perchlorate.

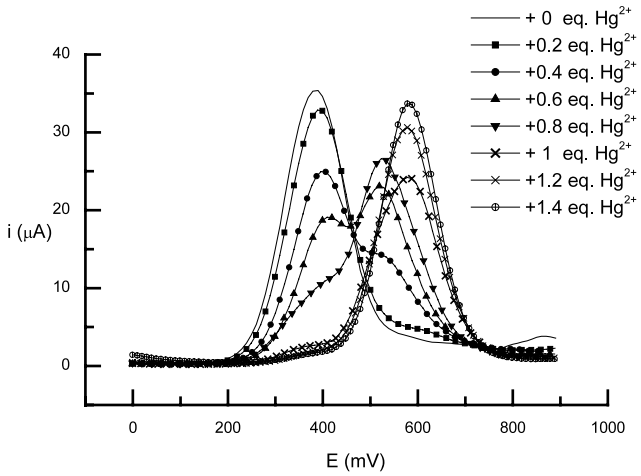


Fig. 3. Cyclic voltammograms and differential pulse voltammetry of L^3 in presence of Hg^{2+} in acetonitrile, 0.1 M tetrabutylammonium perchlorate.

Table 2
Electrochemical response (ΔE in mV) for L^1, L^2, L^3, L^4, and L^5 vs. selected cations in acetonitrile in 0.1 M tetrabutylammonium perchlorate

Receptor	H^+	Ni^{2+}	Cu^{2+}	Zn^{2+}	Cd^{2+}	Hg^{2+}	Pb^{2+}
L^1	220	215	230	220	120	290	250
L^2	135	140	100	155	90	200	185
L^3	200	110	190	180	–	225	220
L^4	110	<20	40	80	50	110	100
L^5	135	80	80	60	65	80	140

ΔE is defined as E_{pa} (receptor + cation) − E_{pa} (free receptor). Scan rate 100 mV s^{-1}.

macrocyclic receptor 1,4,7,10,13,16-hexa(ferrocenylmethyl)-1,4,7,10,13,16-hexaazacyclooctadecane in acetonitrile:dichloromethane mixtures with a potential shift of ca. 80 mV in the presence of Cu^{2+}, Zn^{2+}, Cd^{2+} and Hg^{2+} [32]. In the presence of Pb^{2+}, L^5 shifts its oxidation potential near 140 mV, which is similar to that observed for L^5 in the presence of *p*-toluenesulfonic acid, suggesting that the electrochemical shift (ΔE) is due to the protonation of L^5 rather than to a co-ordination process. The electrochemical behaviour of L^5 has also been recently studied in dioxane:water mixtures showing this receptor a maximum oxidation potential shifts of ca. 35 mV in the presence of Cu^{2+} and Hg^{2+} [33].

L^4 also shows low oxidation potential shifts in the presence of metal cations. For instance the metal ions Ni^{2+}, Cu^{2+}, and Cd^{2+} gave ΔE lower than 50 mV and a shift of 80 mV was observed in the presence of Zn^{2+}. Upon addition of the metal ions Hg^{2+} and Pb^{2+} the potential shifts were a little bit higher ($\Delta E = 110$ and 100 mV, respectively) but were very close to the electrochemical shift observed for L^4 in the presence of five equivalents of H^+, suggesting that protonation, rather than coordination, occurs.

It is noteworthy that for L^4 and L^5 the potential shifts corresponding to protonation (see Table 1) are larger than those observed in the presence of metal cations (see Table 2). This can be explained bearing in mind that, in these systems, the interaction between the guest and the ferrocene/ferrocenium couple is electrostatic. Therefore, for a molecule containing a certain number of ferrocene units, the redox shift observed would depend on the number of charges (metal ion, protons, etc.) and the distance between these charged groups and the ferrocene signalling units. When L^4 and L^5 are fully protonated the electrochemical shift is due to the presence of five positively charged ammonium groups that induce the oxidation potential of the ferrocenyl groups to be anodically shifted. In the presence of metal ions the shift is induced by the presence of the positively charged M^{2+} cations co-ordinated to the N-donor amino groups. As the charge of the cations are lower than that reached when the receptors are fully protonated, then a larger redox shift is observed in the presence of protons than with metal ions.

Receptors L^1, L^2 and L^3 show a very different behaviour and a much larger electrochemical shift in the presence of metal ions. In fact there are some interesting results in the presence of heavy toxic metal ions of environmental importance. Thus, in the presence of Hg^{2+} and Pb^{2+} a maximum shift of the oxidation potential of 290 mV for mercury and of 250 mV for lead is observed with L^1. Both metals produce a two-wave behaviour. The addition of increasing amounts of Hg^{2+} or Pb^{2+} results in the appearance of a new wave. The current associated with the new redox couple increases linearly with the concentration of Hg^{2+} or Pb^{2+} cations until a full equivalent has been added. At this point, the original wave disappears and the new redox couple reaches full development. This observation suggests the formation of 1:1 complexes between L^1 and Hg^{2+} or Pb^{2+}. The electrochemical shift of ca. 300 mV is quite large and suggests a potential application in the development of amperometric sensors. The redox shift corresponding to L^1 upon addition of Ni^{2+} ($\Delta E = 215$ mV) and Zn^{2+} ($\Delta E = 220$ mV) is very close to that obtained by protonation of the receptor L^1, suggesting that the electrochemical shift we are observing is due to protonation and not to coordination.

The L^2 receptor also shows the largest redox shift in the presence of the Hg^{2+} and Pb^{2+} metal ions with electrochemical shifts of 200 and 185 mV, respectively. The cations Cd^{2+} and Cu^{2+} gave lower shifts of the redox potential (90 and 100 mV, respectively) whereas the presence of Ni^{2+} and Zn^{2+} appears to promote protonation (see Table 2).

Receptor L^3 displays large potential shifts of 225 and 220 mV in the presence of Hg^{2+} and Pb^{2+}, respectively. Fig. 3 shows the two-wave behaviour observed

by differential pulse voltammetry upon addition of Hg^{2+} to acetonitrile solutions of L^3. L^3 also shows a two-wave behaviour upon addition of the metal cations Cu^{2+} and Pb^{2+}. In contrast, L^3 shows a continuous shift of the redox potential when increasing amounts of Ni^{2+} or Zn^{2+} are added to solutions of the receptor, with shifts of 115 and 180 mV, respectively. In general these results are in agreement with those reported in an aqueous–organic environment in which L^3 also showed the largest redox shift upon addition of mercury or lead [24].

One of our goals in this field is the design of redox-active receptors showing selectivity and a large electrochemical shift in the presence of toxic heavy metal ions. In this sense the studies described above and summarised in Table 2 gave some information regarding host design and selectivity. Receptors L^1, L^2 and L^3 gave for Hg^{2+} and Pb^{2+} very large electrochemical shifts up to 290 mV for Hg^{2+} and L^1 as receptor, whereas the redox response of receptors L^4 and L^5 to these metals is much lower. The use of aza-oxa binding sites instead of polyazaalkanes enhances the selective electrochemical sensing of heavy metal ions of environmental importance such as Hg^{2+} and Pb^{2+} versus other less-toxic metal cations. It is also noticeable that the largest redox shift in the presence of Hg^{2+} and Pb^{2+} is observed for L^1, the receptor containing the smallest number of both N donor atoms and ferrocenyl signalling subunits.

The electrochemical shift to more positive potentials can be thought of as an increase in the difficulty for the receptor to lose its electrons because of a positively charged ion located in close proximity to the ferrocene group. An alternative is to consider the oxidation process as a switching process that affects the binding properties of the ligand. In this interpretation, the presence of a positive charge in the ferrocene group upon oxidation exerts repulsion against the cation coordinated by the binding sites. This electrostatic repulsion induces a drastic decrease of the binding stability constant and therefore a decrease of the affinity of the ligand for a certain cation. This affinity that can be in principle switched on and off by oxidation and reduction of the electroactive group. It can be demonstrated that in systems showing a two-wave behaviour, the electrochemical shift is related with the ratio K_{red}/K_{ox} where K_{red} is the formation stability constant of the complex in its 'reduced' form and K_{ox} the formation stability constant of the complex in its oxidised form. From the electrochemical shift (ΔE) the quotient K_{red}/K_{ox} can be calculated using the equation $\Delta E = (RT/nF)(ln(K_{red}/K_{ox})$. As stated above the largest electrochemical shift has been obtained for L^1 in the presence of Hg^{2+} and Pb^{2+}. For these two metal ions K_{red}/K_{ox} is 8.01×10^5 and 1.70×10^4, respectively. That means that L^1 binds ca. 10^6 times more strongly the Hg^{2+} cation in acetonitrile than it does its oxidised $(L^1)^+$ form.

3.2. Electrochemical behaviour in the presence of anions

The electrochemical behaviour in the presence of the anions Cl^-, Br^-, HSO_4^- and $H_2PO_4^-$ was studied. Cyclic voltammetry (CV) was carried out in acetonitrile, freshly distilled from CaH_2, with tetrabutylammonium perchlorate as supporting electrolyte. The electrochemical behaviour with anions was recorded after progressive addition of stoichiometric equivalents of anionic guest as their tetrabutylammonium salts. The results are gathered in Table 3. Data for L^3, L^4 and L^5 have been recently published. [25,34]

When ferrocene-functionalised receptors react with anions in non-aqueous solvents such as acetonitrile several type of behaviour have been reported. [25] For instance, both the cathodic or anodic peaks of the reversible Fc/Fc^+ couple can be affected by the presence of anions that usually cause both oxidation and reduction peaks of the ferrocene to be cathodically shifted. The electrochemical shift of the oxidation peak of the ferrocenyl group to more negative potentials is attributed to the interaction of the receptor with the corresponding anion. An additional effect that could be observed is the cathodic shift of the reduction wave of the ferrocenyl groups upon addition of anionic guests. This is generally attributed to the additional strong interaction between the anionic guest and the Fc^+ cations produced upon oxidation. [25]

The addition of Bu_4NBr or Bu_4NCl to solutions of L^1, L^2, L^3, L^5 and L^6 does not induce any electrochemical shift. In contrast the electrochemical response in the presence of sulfate and phosphate is much more pronounced.

In the presence of sulfate, L^4 is the only receptor for which a significant shift of the oxidation potential of the ferrocenyl groups (ΔE_{pa}) is observed. The other L^1, L^2, L^3, L^5 and L^6 receptors do not show any oxidation potential shift upon sulfate addition. In contrast sulfate is able to induce cathodic shifts of the ferrocenyl reduction peak (ΔE_{pc}) in all receptors except L^1. The anion $H_2PO_4^-$ induces larger electrochemical shift, in both the cathodic and the anodic peak of the ferrocenyl groups, than sulfate. The largest shift in the presence of phosphate was observed for L^5 with values of ΔE_{pa} and ΔE_{pc} of 200 and 600 mV, respectively. As an example, Fig. 4 shows the cyclic voltammograms of L^2 upon addition of two, four, six and ten equivalents of the anion $H_2PO_4^-$. In general, the voltammograms of L^3, L^4, L^5 and L^6 ligands upon addition of dihydrogenophosphate show a behaviour similar to that found for L^2. The voltammogram in Fig. 4 upon addition of ten equivalents of $H_2PO_4^-$ is typical of an EC mechanism. Addi-

tionally, the sharp reduction and oxidation peaks that are usually observed are strongly indicative of product adsorption.

From the data in Table 3, some conclusions regarding molecular design for anion recognition can be obtained. For instance when ferrocene-functionalised amines (L) interact with an anion such as $H_2PO_4^-$, the transfer of at least one proton would be expected to give the complex $HL^+-HPO_4^{2-}$. This complex is an anion and its oxidation potential would be expected to be lower than that of the neutral L ligand. In this sense, it would be predicted that the shift of the oxidation potential of the ferrocenyl groups (ΔE_{pa}) would be larger when the number of amino groups is larger. This seems to be the observed trend in Table 2, in which the largest ΔE_{pa} in the presence of phosphate is found for receptors L^4 and L^5 containing four and five amino groups, respectively. The trend in the shift of the reduction peak of the ferrocenyl group ΔE_{pc} is less clear, one would expect ΔE_{pc} to be larger when the number of ferrocenyl centres were larger. However, this does not seem to be the case. Other factors such as the ferrocene–anion distances, and the adsorption processes that can control the position of the reduction peak must also have influence in the value of ΔE_{pc}.

In order to compare the selectivity of L^2, L^5 or L^6 for the four anions Cl^-, Br^-, HSO_4^- and $H_2PO_4^-$, competition experiments were performed. The electrochemical response of L^2, L^5 or L^6 in the presence of $H_2PO_4^-$, even in the presence of a ten fold excess of other anions (sulfate or chloride), is similar to that observed in the presence of $H_2PO_4^-$ alone, indicating that these receptors electrochemically and selectively sense the presence of this anion in acetonitrile.

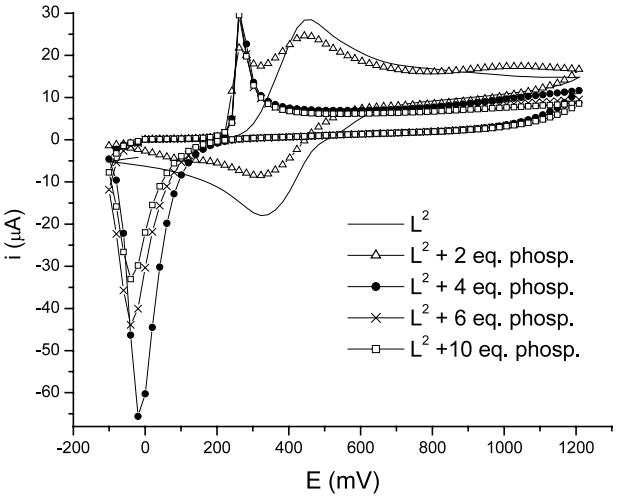


Fig. 4. Cyclic voltammograms of L^2 in presence of $H_2PO_4^-$ in acetonitrile, 0.1 M tetrabutylammonium perchlorate.

Table 3
Electrochemical anion response of L^1, L^2, L^3, L^4, L^5 and L^6 upon addition of 10 equivalents of HSO_4^- or $H_2PO_4^-$ in acetonitrile in 0.1 M tetrabutylammonium perchlorate

Receptor	HSO_4^-		$H_2PO_4^-$	
	ΔE_{pa}	ΔE_{pc}	ΔE_{pa}	ΔE_{pc}
L^1	<5	<5	<5	160
L^2	<5	85	190	346
L^3	<5 [a]	240	85 [a]	370
L^4	145 [b]	380	198 [b]	510
L^5	<5 [a]	230	200 [a]	600
L^6	<5	222	135	556

ΔE_{pa} calculated as E_{pa} of the receptor $-E_{pa}$ of the receptor $-$anion and $\Delta E_{pc} = E_{pc}$ receptor $-E_{pc}$ receptor $-$anion in mV.
[a] From Ref. [25].
[b] From Ref. [34].

4. Conclusion

In summary, it has been shown that redox-active ferrocene-functionalised receptors can, through an electrochemical response, detect target cations and anions in non-aqueous environments. A combination of coordination properties and suitable redox groups has proved to be a good method to strategically design new receptors for the electrochemical recognition of the Hg^{2+} and Pb^{2+} toxic heavy metal ions in non-aqueous solution. The strategy followed includes the selection of suitable binding sites such as aza-oxa derivatives and their functionalisation with ferrocenyl groups. The importance of the molecular design can be noted when compared the electrochemical response for different molecular architectures. In the presence of metal ions two types of responses have been found; a gradual potential shift of the redox couple, or a two-wave behaviour. In the presence of anions only HSO_4^- and $H_2PO_4^-$ display a significant electrochemical shift. For these two anions both cathodic shift of the oxidation (ΔE_{pa}) and reduction (ΔE_{pc}) peaks of the ferrocenyl groups have been observed. The electrochemical studies suggest that there is a selective sensing response for phosphate over sulfate, chloride and bromide. Further work will address with the immobilisation of these or related redox-active receptors on an electrode surface, with a view of constructing molecular electrochemical sensors.

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References

[1] P.L. Boulas, M. Gómez-Kaifer, L. Echegoyen, Angew. Chem. Int. Ed. Engl. 37 (1998) 216.
[2] P.D. Beer, Chem. Soc. Rev. 18 (1989) 409.
[3] R. Martínez-Máñez, J. Soto, J.M. Lloris, T. Pardo, Trends Inorg. Chem. 5 (1998) 183.
[4] J. Janata, M. Josowicz, P. Vanysek, D.M. DeVaney, Anal. Chem. 70 (1998) 179R.
[5] S.R. Miller, D.A. Gustowski, Z.-H. Chen, G.W. Gokel, L. Echegoyen, A.E. Kaifer, Anal. Chem. 60 (1988) 2021.
[6] B. Dietrich, Pure Appl. Chem. 65 (1993) 147.
[7] M.W. Hosseini, A.J. Blacker, J.-M. Lehn, J. Am. Chem. Soc. 112 (1990) 3896.
[8] D.M. Rudkevich, W.P.R.V. Stauthamer, W. Verboom, J.F.J. Engbersen, S. Harkema, D.N. Reinhoudt, J. Am. Chem. Soc. 114 (1992) 9671.
[9] P.D. Beer, A.R. Graydon, A.O.M. Johnson, D.K. Smith, Inorg. Chem. 36 (1997) 2112.
[10] J.E. Kingston, L. Ashford, P.D. Beer, M.G.B. Drew, J. Chem. Soc. Dalton Trans. (1999) 251.
[11] P.D. Beer, Acc. Chem. Res. 31 (1998) 71.
[12] P.D. Beer, P.A. Gale, G.Z. Chen, J. Chem. Soc. Dalton Trans. (1999) 1897.
[13] J.C. Medina, T.T. Godnow, M.T. Rojas, J.L. Atwood, B.C. Lynn, A.E. Kaifer, G.W. Gokel, J. Am. Chem. Soc. 114 (1992) 10583.
[14] M.E. Padilla-Tosta, R. Martínez-Máñez, T. Pardo, J. Soto, M.J.L. Tendero, Chem. Commun. (1997) 887.
[15] J.M. Lloris, R. Martínez-Máñez, T. Pardo, J. Soto, M.E. Padilla-Tosta, Chem. Commun. (1998) 837.
[16] J.M. Lloris, A. Benito, R. Martínez-Máñez, M.E. Padilla-Tosta, T. Pardo, J. Soto, M.J.L. Tendero, Helv. Chim. Acta 81 (1998) 2024.
[17] P.D. Beer, J. Cadman, J.M. Lloris, R. Martínez-Máñez, M.E. Padilla, T. Pardo, D.K. Smith, J. Soto, J. Chem. Soc. Dalton Trans. (1999) 127.
[18] P.D. Beer, Z. Chen, M.G.B. Drew, A.O.M. Johnson, D.K. Smith, P. Spencer, Inorg. Chim. Acta 246 (1996) 143.
[19] P.D. Beer, Z. Chen, M.G.B. Drew, D.K. Smith, J. Organomet. Chem. 543 (1997) 259.
[20] P.D. Beer, Z. Chen, M.G.B. Drew, J. Kingston, M. Ogden, P. Spencer, J. Chem. Soc. Chem. Commun. (1993) 1046.
[21] H. Plenio, C. Aberle, Chem. Commun. (1998) 2697.
[22] J.M. Lloris, R. Martínez-Máñez, T. Pardo, J. Soto, M.E. Padilla-Tosta, Chem. Commun. (1998) 837.
[23] J.M. Lloris, R. Martínez-Máñez, M.E. Padilla-Tosta, T. Pardo, J. Soto, P.D. Beer, J. Cadman, D.K. Smith, J. Chem. Soc. Dalton Trans. (1999) 2359.
[24] J.M. Lloris, R. Martínez-Máñez, M. Padilla-Tosta, T. Pardo, J. Soto, M.J.L. Tendero, J. Chem. Soc. Dalton Trans. (1998) 3657.
[25] P.D. Beer, J. Cadman, J.M. Lloris, R. Martínez-Máñez, J. Soto, T. Pardo, J. Chem. Soc. Dalton Trans. (2000) 1805.
[26] P.D. Beer, D.K. Smith, J. Chem. Soc. Dalton Trans. (1998) 417.
[27] H. Plenio, H. El-Desoky, J. Heinze, Chem. Ber. 126 (1993) 2403.
[28] H. Plenio, J. Yang, R. Diodone, J. Heinze, Inorg. Chem. 33 (1994) 4098.
[29] The dielectric constant of the dioxane:water 70:30 v/v mixture has been calculated as $\varepsilon = \Sigma_i X_i \varepsilon_i$, where X_i and ε_i are the molar fractions and permittivities of water and dioxane.
[30] A. Benito, R. Martínez-Máñez, J. Soto, M.J.L. Tendero, J. Chem. Soc. Faraday Trans. 93 (1997) 2175.
[31] A. Benito, J.M. Lloris, R. Martínez-Máñez, J. Soto, Polyhedron 17 (1998) 491.
[32] J.M. Lloris, R. Martínez-Máñez, J. Soto, T. Pardo, M.E. Padilla-Tosta, A. Benito, M.D. Marcos, Polyhedron 18 (1999) 3689.
[33] To be published.
[34] J.M. Lloris, R. Martínez-Máñez, M.E. Padilla-Tosta, T. Pardo, J. Soto, Helv. Chim. Acta 82 (1999) 1445.