DALTON
FULL PAPER

Anion interaction with ferrocene-functionalised cyclic and open-chain polyaza and aza-oxa cycloalkanes

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Received 6th January 2000, Accepted 24th March 2000

A family of ferrocene-functionalised receptors of different topologies have been used as receptors for anions. The compounds have been designed to contain both amine nitrogen and ether oxygen atoms and comprises from monoaza to pentaaza derivatives both open-chain (L^1, L^2, L^3) or cyclic (L^4, L^5) and having from one to five ferrocenyl groups. Solution studies directed to determine the protonation constants of L^1, L^2 and L^3 have been carried out in water (0.1 mol dm^{-3} KNO_3, 25 °C) and those of L^4 and L^5 in 1,4-dioxane–water (70 : 30 v/v, 0.1 mol dm^{-3} KNO_3, 25 °C). The protonation behaviour of the receptors can be explained taking into account electrostatic considerations. Speciation studies in the presence of phosphate have been carried out in water for L^1, L^2 and L^3 and in dioxane–water for L^4 and L^5. Speciation studies have also been performed in the presence of ATP with L^1, L^2 and L^3 in water. Selectivity of a mixture of receptors against a certain anion is discussed in terms of ternary diagrams. The shift of the redox potential of the ferrocenyl groups as a function of the pH has been studied. The difference between the oxidation potentials at basic and acidic pH has been determined experimentally and is compared with that theoretically predicted using an electrostatic model previously reported. The electrochemical shift in the presence of ATP and phosphate has been measured in water for L^1, L^2 and L^3 and in the presence of phosphate and sulfate in 1,4-dioxane–water for L^4 and L^5 as a function of the pH. The electrochemical response found against those anions is quite poor with maximum cathodic shifts of *ca*. 30–40 mV. The electrochemical response induced by HSO_4^- and $H_2PO_4^-$ has also been studied in acetonitrile solutions where a large cathodic shift for $H_2PO_4^-$ up to *ca*. 200 mV was found.

Introduction

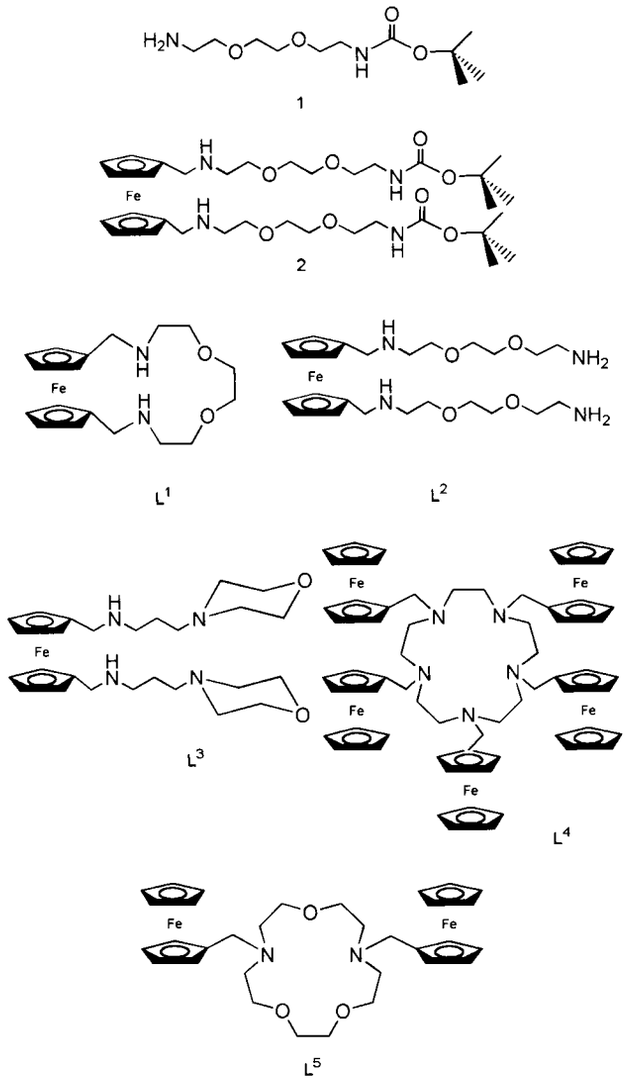
Designing of molecules containing appropriate signalling subunits has been a synthetic strategy for the development of new sensing receptors of application in sensor technologies. In these systems, co-ordination of the target guest to the binding sites followed by a further interaction of the complex with the covalently attached signalling subunits allows transformation of chemical information into a measurable signal. The possibility of modulation of the co-ordination sites, the nature and number of signalling units (bearing in mind that external factors such as for example the solvent may also influence) makes the number of potential receptors very large and the search for selective receptors against target substrates a challenge. Among different signalling subunits described in the literature there is an increasing interest for redox-active groups.[1–7] In these systems the signalling effect is based on the fact that co-ordination can induce a shift of the redox potential of the electroactive subunits. A number of works have allowed the synthesis of suitable and selective receptors that electrochemically can recognise cationic,[8–16] anionic[17–21] and neutral[22,23] molecules. New advances in this area would probably involve the use of different not well studied redox-active units and the search for potential applications as electrochemical sensors based on amperometric measurements. With the aim of advance in the knowledge of redox-active ferrocene-functionalised systems and taking into account that relatively little effort has been devoted to the study of their anion sensing ability in water,[24–39] we report here a solution and electrochemical study on a family of new receptors in the presence of some anions such as ATP, phosphate and sulfate. The receptors have been designed to contain both amine nitrogen and ether oxygen atoms and comprise from monoaza to pentaaza derivatives both open-chain or cyclic, having from one to five ferrocenyl groups.

Experimental

Physical measurements

Potentiometric titrations were carried out in water (0.1 mol dm^{-3} KNO_3) for L^1, L^2 and L^3 and in 1,4-dioxane–water (70 : 30 v/v, 0.1 mol dm^{-3} KNO_3) for L^4 and L^5 using a reaction vessel water-thermostatted at 25.0 ± 0.1 °C under a nitrogen atmosphere. Experimental potentiometric details have been published previously.[36] The concentration of the metal ions was determined using standard methods. The computer program SUPERQUAD[40] was used to calculate the protonation and stability constants. The titration curves for each system (*ca*. 250 experimental points corresponding to at least three titration curves, pH = −log [H] range investigated 2.5–10, concentration of the ligand and metal ion being *ca*. 1.2×10^{-3} mol dm^{-3}) were treated either as a single set or as separated entities without significant variations in the values of the stability constants. Finally the data sets were merged and treated simultaneously to give the stability constants. Electrochemical data were obtained in water, 1,4-dioxane–water (70 : 30 v/v) and in dry acetonitrile, with a programmable function generator Tacussel IMT-1, connected to a Tacussel PJT 120–1 potentiostat. The working electrode was platinum with a saturated calomel reference electrode separated from the test solution by a salt bridge

DOI: 10.1039/b000079p



containing the solvent/supporting electrolyte. The auxiliary electrode was platinum wire.

Syntheses

***N*-*tert*-Butoxycarbonyl-2,2′-ethylenedioxybis(ethylamine) 1.** The following procedure was similar to that described in reference 41. Di(*tert*-butoxycarbonyl) (2.45 g, 0.011 mol) was dissolved in 30 mL of 1,4-dioxane. This was added to 12.50 g of 2,2′-(ethylenedioxy)bis(ethylamine) (0.085 mol) also dissolved in 30 mL of 1,4-dioxane, over 2.5 hours. The mixture was stirred for 24 hours after which the solvent was removed on a rotary evaporator giving a white semi-solid. Water (50 mL) was added and the white precipitate of the bis-substituted by-product subsequently filtered off. The aqueous filtrate was extracted with 3 × 50 mL of dichloromethane. This organic layer was backwashed with 2 × 10 mL of water to remove any excess of diamine, then dried with $MgSO_4$, filtered and reduced in vacuum resulting in a clear viscous oil. Yield 1.97 g, 70% (Found: C, 52.24; H, 10.23; N, 10.51. $C_{11}H_{24}N_2O_4·0.5H_2O$ requires C, 51.34; H, 9.79; N, 10.89%). NMR ($CDCl_3$, TMS): ^{1}H, δ 1.12 (br, 2 H, NH), 1.19 (s, 9 H, ^{t}Bu), 2.63 (t, 2 H, CH_2NH_2), 3.07 (m, 2 H, CH_2NHCO), 3.28 (t, 2 H, OCH_2), 3.31 (t, 2 H, OCH_2), 3.38 (s, 4 H, OCH_2CH_2O) and 5.28 (br, 1 H, NHCO). FABMS: *m*/*z* 249 $[M + H]^+$.

***N*-(1,1′-Bis(methyl)ferrocene)-*N*′-*tert*-butoxycarbonyl-2,2′-ethylenedioxybis(ethylamine) 2.** Ferrocene-1,1′-dicarbaldehyde (0.25 g, 1.03 mmol) in 30 mL of dry acetonitrile was added to 0.51 g of *N*-*tert*-butoxycarbonyl-2,2′-ethylenedioxybis(ethylamine) **1** (2.05 mmol), also in 30 mL of acetonitrile, and stirred overnight under a nitrogen atmosphere and darkness. The solution was evaporated and then methanol and small portions of sodium tetrahydroborate (to a fivefold excess) were added and the mixture was stirred for 3 hours. After removal of methanol on a rotary evaporator, 40 mL of dichloromethane were added and the off-white inorganic solid filtered off. The dichloromethane was then evaporated and the organic oil taken up in 50 mL of acetone and refluxed for 2.5 hours. After cooling, any further solid was filtered off to give the crude product as a viscous orange oil. Purification was achieved with a silica gel column using methanol–aqueous ammonia (99 : 1 v/v) as eluent. The main yellow fraction was collected and concentrated to an orange oil. Yield 0.51 g, 70%. ^{1}H NMR ($CDCl_3$, TMS): δ 1.44 (s, 18 H, ^{t}Bu), 2.82 (t, 4 H, CH_2N), 3.27 (m, 4 H, CH_2NHCO), 3.50 (s, 4 H, Cp CH_2N), 3.58 (s, 16 H, OCH_2), 4.07 (d, 4 H, Cp H), 4.15 (d, 4 H, Cp H) and 5.21 (br, 2 H, NHCO).

1,1′-Bis(10-amino-5,8-dioxa-2-azadecyl)ferrocene L^2. The *tert*-butoxycarbonyl of compound **2** was removed by adding 5 mL of trifluoroacetic acid to **2** (0.49 g) dissolved in 10 mL of dichloromethane at room temperature. After stirring for thirty minutes, the solvent was removed and the salt subsequently neutralised with 1 mol dm^{-3} KOH. The water was removed and then the yellowish solid triturated with hot dichloromethane to afford the free amine in 70% yield. The compound was converted into the hydrochloride salt in quantitative yield by bubbling HCl(g) through a dry diethyl ether solution of it. Found: C, 42.99; H, 7.10; N, 7.83. $C_{24}H_{46}Cl_4FeN_4O_4·H_2O$ requires C, 43.00; H, 7.22; N, 8.36%). NMR (CD_3OD): ^{1}H, δ 3.06 (t, 4 H, CH_2N), 3.10 (t, 4 H, NCH_2), 3.63 (s, 8 H, OCH_2-CH_2O), 3.66 (m, 8 H, NCH_2CH_2O), 4.09 (s, 4 H, $CpCH_2N$), 4.32 (d, 4 H, Cp H) and 4.48 (d, 4 H, Cp H); ^{13}C, δ 40.60 (NCH_2), 47.36 (NCH_2), 48.17 (NCH_2), 66.91 (CH_2O), 67.82 (CH_2O), 71.32 (OCH_2CH_2O), 71.35 (OCH_2CH_2O), 71.86 (Cp), 72.81 (Cp) and 78.34 (C_{ipso} of Cp). Electrospray MS: *m*/*z* 507, $[M - 3HCl]^+$; 529, $[M - 3HCl + Na]^+$; and 543 $[M - 4HCl]^+$.

1,1′-Bis(5-morpholino-2-azapentyl)ferrocene L^3. Ferrocene-1,1′-dicarbaldehyde (0.24 g, 0.99 mmol) in 25 mL of dry acetonitrile was added to 0.28 g of 4-morpholino-1-azabutane (1.94 mmol) in 25 mL of dry acetonitrile with 4 Å molecular sieves, and then stirred overnight under nitrogen in the dark. The resulting dark orange solution was filtered and washed with a small amount of chloroform. The solution was evaporated to an orange oil which was then reduced in methanol with a fivefold excess of sodium tetrahydroborate for three hours. The work-up procedure was as for L^2 using 95 : 5 v/v methanol–ammonia as eluent. Yield 0.31 g, 64%. Found: C, 45.08; H, 7.73; N, 7.86. $C_{26}H_{46}Cl_4FeN_4O_2·3H_2O$ requires C, 44.72; H, 7.50; N, 8.02%). NMR ($CDCl_3$): ^{1}H, δ 1.42 (bs, 2 H, NH), 1.64 (tt, 4 H, CCH_2C), 2.35 (t, 4 H, NCH_2), 2.39 (bs, 8 H, NCH_2(morph)), 2.63 (t, 4 H, $NHCH_2$), 3.47 (s, 4 H, $CpCH_2N$), 3.67 (bs, 8 H, OCH_2), 4.03 (d, 4 H, C pH) and 4.09 (d, 4 H, C pH); ^{13}C, δ 26.75 (CCH_2C), 47.99 (NCH_2), 48.95 (NCH_2), 53.75 (NCH_2CH_2O), 57.23 (CH_2(morph)), 66.93 (CH_2O), 68.25 (Cp), 68.82 (Cp), 86.96 (C_{ipso} of Cp). FABMS: *m*/*z* 535, $[M - 4HCl]^+$; and 499, $[M - 3HCl]^+$.

1,4,7,10,13-Penta(ferrocenylmethyl)-1,4,7,10,13-pentaazacyclopentadecane, L^4. 1,4,7,10,13-Pentaazacyclopentadecane (0.4 g, 1.86 mmol) and 4.29 g (11.16 mmol) of (ferrocenylmethyl)trimethylammonium iodide[42] were heated to reflux in acetonitrile (300 mL) for 4 days in the presence of sodium carbonate (6 g). The warm reaction mixture was filtered and the yellow solution evaporated to dryness. The resulting solid was dissolved in dichloromethane and chromatographed using dichloromethane–methanol (99 : 1) as eluent. Further recrystallisation in dichloromethane–hexane gave L^4 as an orange solid (700 mg, 30%) (Found: C, 62.24; H, 6.36; N, 5.48. $C_{65}H_{75}$-

Table 1 Stepwise protonation constants for L^1, L^2, L^3, L^4 and L^5. Water (25 °C, 0.1 mol dm^{-3} potassium perchlorate) was used for L^1, L^2 and L^3, dioxane–water (70 : 30 v/v, 25 °C, 0.1 mol dm^{-3} potassium nitrate) for L^4 and L^5

	L^1	L^2	L^3	L^4	L^5
$L + H^+ \rightleftharpoons [HL]^+$	9.57(1)[a]	9.97(1)	10.18	9.38(2)	8.40(2)
$L + 2H^+ \rightleftharpoons [H_2L]^{2+}$	17.81(2)	19.85(1)	19.61	16.43(2)	15.09(3)
$L + 3H^+ \rightleftharpoons [H_3L]^{3+}$	—	28.79(2)	26.11	21.34(3)	
$L + 4H^+ \rightleftharpoons [H_4L]^{4+}$	—	37.68(2)	31.93	24.42(3)	
$L + 5H^+ \rightleftharpoons [H_5L]^{5+}$	—	—	—	26.76(4)	
$[HL]^+ + H^+ \rightleftharpoons [H_2L]^{2+}$	8.24	9.88	9.43	7.05	6.69
$[H_2L]^{2+} + H^+ \rightleftharpoons [H_3L]^{3+}$	—	8.94	6.50	4.91	
$[H_3L]^{3+} + H^+ \rightleftharpoons [H_4L]^{4+}$	—	8.89	5.82	3.08	
$[H_4L]^{4+} + H^+ \rightleftharpoons [H_5L]^{5+}$	—	—		2.34	

[a] Values in parentheses are the standard deviations in the last significant digit.

$Fe_5N_5{\cdot}3H_2O$ requires C, 62.00; H, 6.43; N, 5.56%). NMR ($CDCl_3$): ^1H, δ 4.10, 4.09 (two br resonances, 45 H, C_5H_5 and C_5H_4), 3.36 (br, 10 H, CH_2) and 2.43 (br, 20 H, CH_2); ^{13}C-{^1H}, δ 83.40 (C_{ipso}, C_5H_4), 70.20, 67.80 (C_5H_4), 68.41 (C_5H_5), 54.13 (CH_2) and 51.12 (CH_2). Mass spectrum (FAB): *m/z* 1205 (M^+).

Results and discussion

The synthesis of receptors L^1 and L^5 has been published elsewhere (see reference 43). The synthesis of L^2 has been carried out by reaction of ferrocene-1,1′-dicarbaldehyde with the diamine 2,2′-ethylenedioxybis(ethylamine) that was previously blocked in one amine position with a butoxycarbonyl (BOC) group followed by further reduction of the imine formed and elimination of the BOC group with trifluoroacetic acid. L^3 was synthesized by reaction of the dicarbaldehyde with aminopropylmorpholine to produce a bis-imine that was reduced with $NaBH_4$ by using standard procedures. The synthesis of L^4 was carried out by reaction of 1,4,7,10,13-pentaazacyclopentadecane with an excess of (ferrocenylmethyl)trimethylammonium iodide in acetonitrile in the presence of sodium carbonate. ^1H, ^{13}C NMR, mass spectra and elemental analysis of L^2, L^3 and L^4 were consistent with the proposed formulations.

L^1 to L^5 are a family of redox-functionalised polyaza or aza-oxa receptors showing a variety of topologies from cyclic to open-chain and having from one to five ferrocenylmethyl groups. It is well known that polyammonium receptors can interact with anions *via* electrostatic effects or by formation of hydrogen bonding networks and therefore L^1 to L^5 are candidates to form complexes with anionic guests. Additionally, the presence of redox-active groups near the co-ordination sites could allow receptors L^1 to L^5 electrochemically to sense the presence of anions. Potentiometric and electrochemical studies have been carried out in order to characterise the solution behaviour against selected guests.

Protonation studies

Solution studies directed to the determination of protonation constants and stability constants for the formation of complexes of L^1, L^2, L^3, L^4 and L^5 with anions have been carried out. Data for L^1, L^2 and L^3 have been obtained in water (25 °C, 0.1 mol dm^{-3} KNO_3), whereas data for L^4 and L^5 have been determined in 1,4-dioxane–water (70 : 30 v/v, 25 °C, 0.1 mol dm^{-3} KNO_3) due to their low solubility in water or other solvent mixtures. Protonation constants of receptors L^1 to L^5 are shown in Table 1.

The protonation behaviour of the receptors is as expected and can satisfactorily be explained by taking into account electrostatic considerations. Among the three receptors measured in water, L^2 shows the more basic behaviour. The first protonation constant is similar for all three receptors, whereas the second protonation is less basic for L^1 consistent with the cyclic nature of the ferrocenophane moiety that makes the second protonation occur near an ammonium group. In L^2 and L^3 the free rotation of the cyclopentadienyl rings minimises the charge repulsion effect between ammonium groups. Additionally the small difference between the first two protonation constants suggests that the second proton attacks the arm in L^2 or L^3 that is unprotonated. The difference between the third and fourth protonations of L^2 and L^3 is in accordance with the fact that larger spacers between nitrogens produce larger basicity. The difference between the second and third protonation constants for L^2 is 0.94 logarithm units, whereas the difference between the logarithm of the second and third protonation steps in L^3 is 2.93. The third protonation in L^3 would take place at a nitrogen separated by one propane chain from one already protonated nitrogen, whereas in L^2 the separation between the nitrogen to be protonated and one ammonium group is larger due to the presence of the $(CH_2)_2O(CH_2)_2O(CH_2)_2$ spacer. A similar effect is found when comparing the difference between the third and the fourth protonation basicity constants of L^2 and L^3.

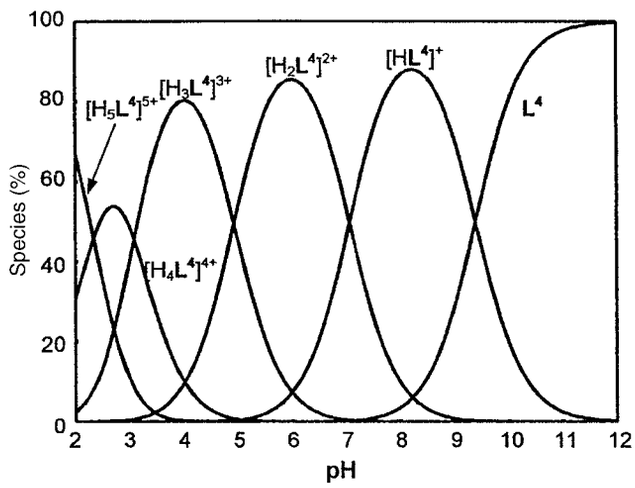


Fig. 1 Distribution diagram of the L^4–H^+ system.

Despite the use of a different solvent, in comparison with L^2 and L^3, its cyclic nature makes L^4 more basic than the open-chain polyamines. For instance the difference between the logarithms of the first and fourth protonation constant of L^2 and L^3 is 1.08 and 4.36, whereas the same difference for L^4 is 6.30. Fig. 1 shows the distribution diagram of the L^4–H^+ system. More detailed protonation studies on polyazaalkanes are usually developed by monitoring ^1H or ^{13}C NMR spectra as a function of the pH.

From a different viewpoint stepwise protonation constants can be calculated using eqn. (1).[44,45] This equation works quite

$$\log \beta_i = i \log K_1 - \left[\frac{e^2 N_A}{2.3RT\pi\varepsilon_0\varepsilon} \sum_{k=1}^{i} \sum_{l=1}^{k-1} \frac{1}{r_{kl}} + B \sum_{k=1}^{i} \sum_{l=1}^{k-1} \frac{1}{r_{kl}^2} \right] \quad (1)$$

well for open-chain polyamines and allows one to predict the overall protonation constants providing that the first protonation is known (K_1). ε represents the macroscopic relative permittivity of the medium and ε_0 the permittivity constant *in vacuo*. The distances r_{kl} between ammonium groups can be obtained by using adequate modelling programs ($B = 30.6$ Å^{-2} in water).[46] The equation assumes that the decrease of the successive protonation constants is mainly due to electrostatic repulsion between ammonium groups. Following this approach the logarithms of the calculated and experimental overall protonation constants for receptors L^1 to L^3 are shown in Table 2. The protonation path assumed is that minimising electrostatic repulsion in each protonation step. There is in general a good agreement between the experimental and calculated protonation constants except for the fourth protonation of L^3.

Anion binding studies

Speciation studies have been carried out in water (0.1 mol dm^{-3}, KNO_3, 25 °C) for L^1, L^2 and L^3 and in 1,4-dioxane–water (70 : 30 v/v, 0.1 mol dm^{-3} KNO_3, 25 °C) for L^1 and L^5. Tables 3 and 4 report the stability constants found for the L–H$^+$–A systems (see Table 3 for phosphate, Table 4 for ATP). Ferrocene-functionalised polyamines have proved to be good receptors for the electrochemical recognition of target anions[4] since (i) polyamines give in aqueous solution highly charged protonated species able to interact with anions *via* electrostatic forces and by formation of hydrogen bonding interactions and (ii) ferrocenium cations formed upon oxidation during electrochemical experiments are also capable of producing favourable electrostatic interactions with anions (see below).[20] Table 3 shows the thermodynamic stability constants found from potentiometric titration experiments in the presence of phosphate for receptors L^1, L^2, L^3, L^4 and L^5. For L^1 three different complexes have been found that may involve the interaction of $[HL^1]^+ + HPO_4^{2-}$, $[H_2L^1]^{2+} + HPO_4^{2-}$ and $[H_2L^1]^{2+} + H_2PO_4^-$. Assuming these interactions between species, the logarithms of the stability constants lie between 2.76 and 3.35 (see Table 3). A similar interpretation appears to be operative for the L^5–H$^+$–phosphate system, although the logarithms of the formation stability constants are larger for L^5 than for L^1.

Logarithms of the protonation constants of L^2 are in the range 9.97 to 8.89. Bearing in mind that the logarithm of the first protonation of phosphate is 12.03 and that the second protonation does not take place until pH 7.03, the existing species in solution are tentatively assigned to the interaction of HPO_4^{2-} with the species $[H_2L^2]^{2+}$, $[H_3L^2]^{3+}$ and $[H_4L^2]^{4+}$. Assuming these interactions, the logarithms of the stability constants for the equilibria $[H_2L^2]^{2+} + HPO_4^{2-} \rightleftharpoons [H_3L^2PO_4]$, $[H_3L^2]^{3+} + HPO_4^{2-} \rightleftharpoons [H_4L^2PO_4]^+$ and $[H_4L^2]^{4+} + HPO_4^{2-} \rightleftharpoons [H_5L^2PO_4]^{2+}$ are 2.43, 2.73 and 2.56, respectively, values that are in the range of those found for the interaction of L^1 with phosphate. Additionally the complex $[H_6L^2PO_4]^{3+}$ has also been found to exist and probably involves $[H_4L^2]^{4+}$ and $H_2PO_4^-$. The last protonation constant of L^3 (log $K = 5.82$ for $[H_3L^3]^{3+} + H^+ \rightleftharpoons [H_4L^3]^{4+}$) is even smaller than the second protonation of phosphate (log $K = 7.03$ for $HPO_4^{2-} +$

Table 2 Calculated and experimental overall protonation constants for the L^1, L^2 and L^3 receptors

Receptor	log β_i(calc.)[a]	log β_i(exp.)[b]
L^1	—	9.57
	17.92	17.81
L^2	—	9.97
	19.68	19.85
	28.88	28.79
	37.14	37.68
L^3	—	10.18
	19.48	19.61
	26.72	26.11
	34.27	31.93

[a] From eqn. (1). [b] From potentiometry.

Table 4 Logarithms of the stability constants for the interaction of L^1, L^2 and L^3 with ATP in water (25 °C, 0.1 mol dm^{-3} KNO_3)

	L^1	L^2	L^3
$L + 2H^+ + ATP^{4-} \rightleftharpoons [H_2LATP]^{2-}$	20.81(2)[a]	23.11(5)	22.63(2)
$L + 3H^+ + ATP^{4-} \rightleftharpoons [H_3LATP]^-$	27.91(2)	32.22(5)	29.98(2)
$L + 4H^+ + ATP^{4-} \rightleftharpoons [H_4LATP]$	32.47(2)	40.72(7)	36.32(2)
$L + 5H^+ + ATP^{4-} \rightleftharpoons [H_5LATP]^+$	—	47.26(9)	42.19(3)
$L + 6H^+ + ATP^{4-} \rightleftharpoons [H_6LATP]^{2+}$	—	—	46.28(4)
$[H_2L]^{2+} + ATP^{4-} \rightleftharpoons [H_2LATP]^{2-}$	3.00	3.26	3.02
$[H_3L]^{3+} + ATP^{4-} \rightleftharpoons [H_3LATP]^-$	—	3.43	3.87
$[H_4L]^{4+} + ATP^{4-} \rightleftharpoons [H_4LATP]$	—	3.04	4.39
$[H_2L]^{2+} + HATP^{3-} \rightleftharpoons [H_3LATP]^-$	3.32	5.59	3.59
$[H_2L]^{2+} + H_2ATP^{2-} \rightleftharpoons [H_4LATP]$	3.87	10.08	5.92
$[H_3L]^{3+} + HATP^{3-} \rightleftharpoons [H_4LATP]$	—	5.15	3.43
$[H_3L]^{3+} + H_2ATP^{2-} \rightleftharpoons [H_5LATP]^+$	—	7.68	5.29
$[H_4L]^{4+} + HATP^{3-} \rightleftharpoons [H_5LATP]^+$	—	2.80	3.48
$[H_4L]^{4+} + H_2ATP^{2-} \rightleftharpoons [H_6LATP]^{2+}$	—	—	3.56

[a] Values in parentheses are the standard deviations in the last significant digit.

Table 3 Logarithms of the stability constants for the interaction of L^1, L^2, L^3, L^4 and L^5 with phosphate in water (25 °C, 0.1 mol dm^{-3} KNO_3) for L^1, L^2, L^3 and in 1,4-dioxane–water (70 : 30 v/v, 25 °C, 0.1 mol dm^{-3} KNO_3) for L^4, L^5

	L^1	L^2	L^3	L^4	L^5
$L + 2H^+ + PO_4^{3-} \rightleftharpoons [H_2LPO_4]^-$	24.36(2)[a]	—	—	—	23.99(2)
$L + 3H^+ + PO_4^{3-} \rightleftharpoons [H_3LPO_4]$	33.02(2)	34.31(9)	34.51(4)	—	32.01(2)
$L + 4H^+ + PO_4^{3-} \rightleftharpoons [H_4LPO_4]^+$	40.22(3)	43.55(7)	42.38(4)	40.31(4)	38.91(1)
$L + 5H^+ + PO_4^{3-} \rightleftharpoons [H_5LPO_4]^{2+}$	—	52.27(9)	48.93(4)	46.48(5)	—
$L + 6H^+ + PO_4^{3-} \rightleftharpoons [H_6LPO_4]^{3+}$	—	60.21(7)	55.70(4)	51.23(5)	—
$[H_2L]^{2+} + PO_4^{3-} \rightleftharpoons [H_2LPO_4]^-$	6.55	—	—	—	8.9
$[H_3L]^{3+} + PO_4^{3-} \rightleftharpoons [H_3LPO_4]$	—	5.52	8.4	—	—
$[H_4L]^{4+} + PO_4^{3-} \rightleftharpoons [H_4LPO_4]^+$	—	5.87	10.45	15.89	—
$[H_5L]^{5+} + PO_4^{3-} \rightleftharpoons [H_5LPO_4]^{2+}$	—	—	—	19.72	—
$[HL]^+ + HPO_4^{2-} \rightleftharpoons [H_2LPO_4]^-$	2.76	—	—	—	3.85
$[H_2L]^{2+} + HPO_4^{2-} \rightleftharpoons [H_3LPO_4]$	3.18	2.43	2.87	—	5.18
$[H_2L]^{2+} + H_2PO_4^- \rightleftharpoons [H_4LPO_4]^+$	3.35	4.64	3.71	3.84	3.52
$[H_3L]^{3+} + HPO_4^{2-} \rightleftharpoons [H_4LPO_4]^+$	—	2.73	4.24	7.23	—
$[H_3L]^{3+} + H_2PO_4^- \rightleftharpoons [H_5LPO_4]^{2+}$	—	4.42	3.76	5.10	—
$[H_4L]^{4+} + HPO_4^{2-} \rightleftharpoons [H_5LPO_4]^{2+}$	—	2.56	4.97	10.32	—
$[H_4L]^{4+} + H_2PO_4^- \rightleftharpoons [H_6LPO_4]^{3+}$	—	3.47	4.71	6.77	—
$[H_5L]^{5+} + HPO_4^{2-} \rightleftharpoons [H_6LPO_4]^{3+}$	—	—	—	12.73	—

[a] Values in parentheses are the standard deviations in the last significant digit.

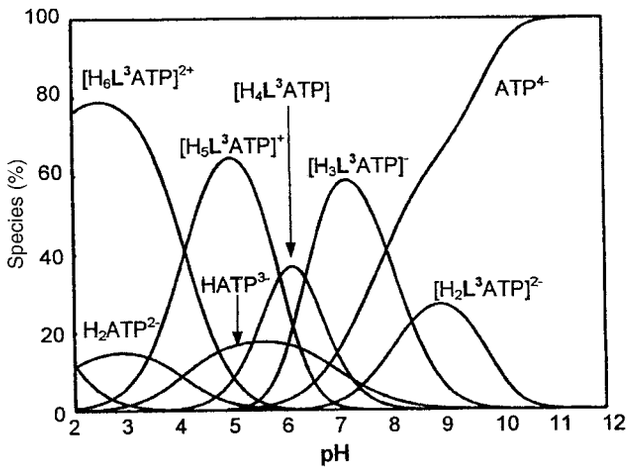


Fig. 2 Distribution diagram of the L^3–H^+–ATP system.

$H^+ \rightleftharpoons H_2PO_4^-$). That makes the determination of the nature of the phosphate complexes rather difficult taking into account only stability constant values.

For the L^4 receptor, even the third protonation of phosphate is larger than the last protonation of the receptor making it again difficult to know the nature of the complexes. Nevertheless the stability constants found in 1,4-dioxane–water for the L^4–H^+–phosphate system seem to be higher than those found for L^2 and L^3 in water. In the case of L^3-phosphate the interaction between PO_4^{3-} and the protonated species, $\log K = 8.40$ for $[H_3L^3]^{3+} + PO_4^{3-} \rightleftharpoons [H_3L^3PO_4]$ and $\log K = 10.45$ for $[H_4L^3]^{4+} + PO_4^{3-} \rightleftharpoons [H_4L^3PO_4]^+$. In the case of the L^4–phosphate system the stability constants for the analogous equilibria are $\log K = 15.89$ and 19.72. The different affinity can be explained by taking into account the reduction of the permittivity in dioxane–water when compared with water. The different topology of the ligands (cyclic *versus* acyclic) and the number of nitrogen atoms also can influence the observed behaviour.

In Table 4 the stability constants of the acyclic L^1, L^2 and L^3 receptors with ATP are reported. Fig. 2 plots the distribution diagram for the L^3–H^+–ATP system. Receptor L^1 and receptor L^2 are fully protonated at pH lower than *ca.* 8, whereas the first protonation of the ATP in water is at *ca.* 6.7 and therefore the complexes expected in solution would involve the interaction of ATP^{4-} with the protonated species H_jL^{j+}. Additionally protonated species of the type $[H_5L^2ATP]^+$ have also been found and probably are related with the interaction of $[H_4L^2]^{4+}$ with $HATP^{3-}$. Spermine $[H_2N(CH_2)_3NH(CH_2)_4NH(CH_2)_3NH_2]$ is an open-chain tetraamine whose interaction with ATP has also been reported in water.[47] In this case the logarithm of the stability constant between the tetraprotonated spermine and the ATP^{4-} was found to be 3.97 which is a value close to that found for the interaction of $[H_4L^2]^{4+}$ and ATP^{4-} ($\log K = 3.04$ for $[H_4L^2]^{4+} + ATP^{4-} \rightleftharpoons [H_4L^2ATP]$).

In order to summarise the interaction of the ligands L^1, L^2, L^3, L^4 and L^5 with phosphate and L^1, L^2 and L^3 with ATP, we have plotted in Fig. 3(a) and 3(b) the formation stability constants of the different $H_jLPO_4^{j-3}$ and H_jLATP^{j-4} species as a function of the number of protons in the complex. To calculate these constants we have proceeded as follows. From the distribution diagrams of the L–H^+–phosphate or L–H^+–ATP systems is determined the pH at which a certain complex $H_jLPO_4^{j-3}$ or H_jLATP^{j-4} is formed. Then, it is assumed that the interaction to give the corresponding complex is established between the L–H^+ and the anion–H^+ species that existed in the highest percentage at this pH. From these plots some information regarding host design and selectivity could be acquired. The formation stability constants against phosphate are higher for L^4 and L^5 than for L^1, L^2 and L^3. This is probably due to the lower relative permittivity of dioxane–water mixtures when compared with that of pure water. Larger formation stability

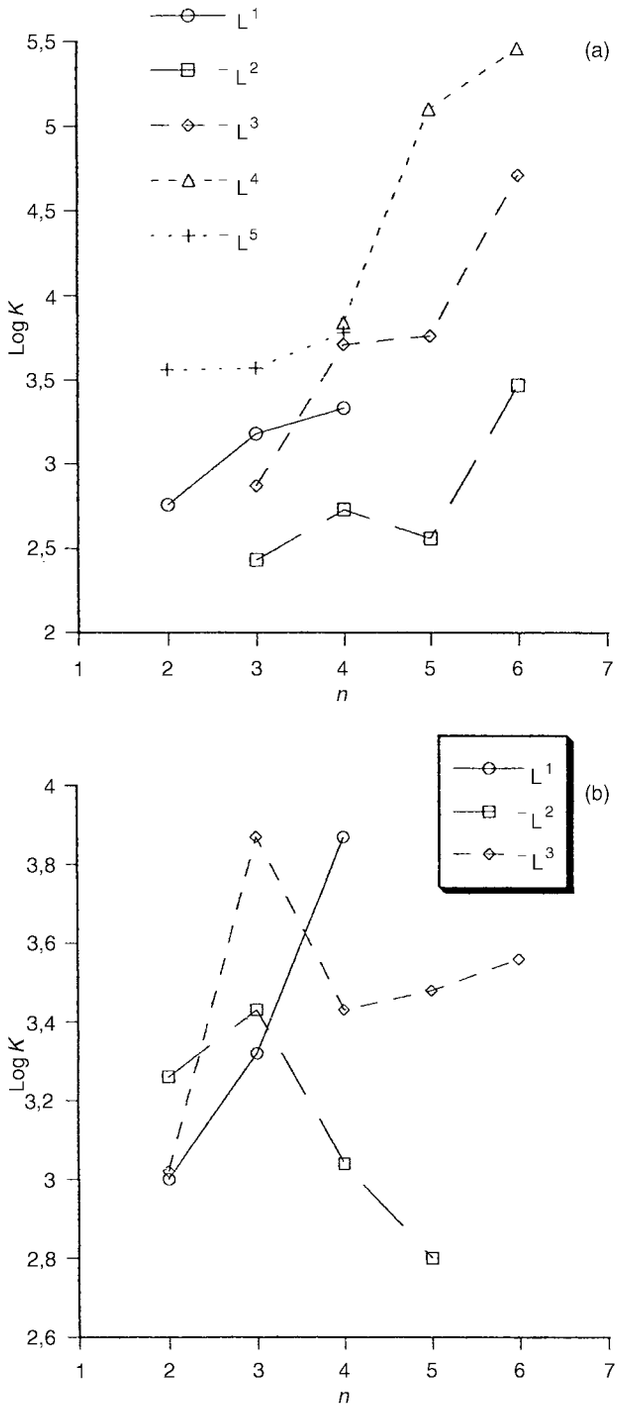


Fig. 3 Formation stability constants (log K) as a function of the number of protons (n) for the interaction of (a) L^1, L^2, L^3, L^4 and L^5 with phosphate and (b) L^1, L^2 and L^3 with ATP.

constants with phosphate are found for the receptor L^4 which is the one containing the largest number of nitrogen atoms. Receptors L^1 and L^5 (both containing two amino groups) display a similar co-ordination behaviour, the stability constants of L^5, obtained in dioxane–water, being slightly larger than those of L^1 in water. Of interest is the comparison between the stability constants of L^2 and L^3 with phosphate. Both receptors contain four amino groups and, despite the larger basicity of L^2 and the presence of oxygen atoms that can give hydrogen bonding interactions with protonated phosphate species, the higher formation stability constants are found for L^3. A similar behaviour is found in the interaction of L^2 and L^3 with ATP; the larger stability constants are obtained with L^3. Molecular modelling of the interaction of L^2 and L^3 with phosphate and ATP showed that the receptor L^3 is able to embrace the sub-

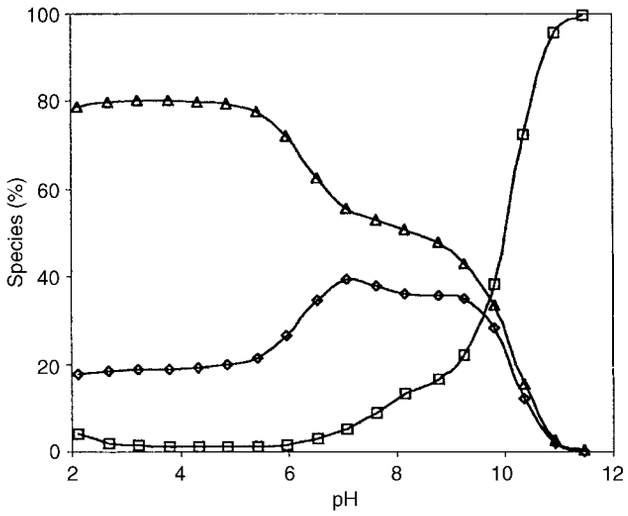


Fig. 4 Distribution diagram of the ternary system L^2, L^3–H^+-phosphate. The sum of percentages of complexed species are plotted *versus* pH. □, Phosphate; ◇, L^2–phosphate; △, L^3–phosphate.

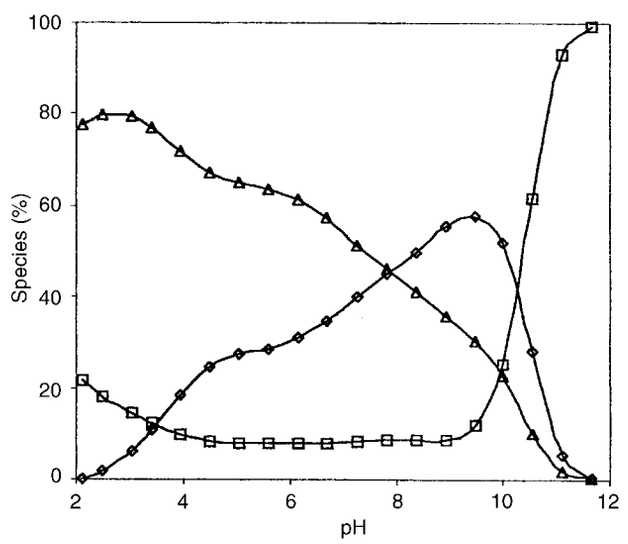


Fig. 5 Distribution diagram of the ternary system L^2, L^3–H^+–ATP. The sum of percentages of complexed species are plotted *versus* pH. □, ATP; ◇, L^2–ATP; △, L^3–ATP.

strates giving interaction with the four basic centres. In contrast L^2 is only able to interact with the two nearest ammonium groups to the ferrocenyl unit, the others being too far from the anion to give a noticeable contact. This is in line with the fact that the largest stability constant found for the interaction of L^2 and phosphate is close to the largest stability constant found for the interaction of L^1 or L^5 (containing two ammonium groups) with phosphate (see Fig. 3). Therefore, the presence of closer amino groups in L^3 separated by a propyl instead of a $(CH_2)_2O(CH_2)_2O(CH_2)_2$ spacer as in L^2 produces a stronger interaction between the anion and the receptor. In order to determine the selectivity in a mixture of L^2 and L^3 in the presence of phosphate, we have plotted the ternary diagram for L^2, L^3–H^+–phosphate (Fig. 4) by means of a calculation of the overall percentages of each receptor bound to the anion as a function of the pH.[48,49] It reveals that there is a selective complexation of phosphate with receptor L^3 especially at acidic pH. To study the selectivity in a mixture of the receptors L^2 and L^3 against ATP we have also plotted diagrams of the ternary systems L^2, L^3–H^+–ATP containing ATP and each receptor (Fig. 5). This reveals the selective complexation of ATP with L^3 at acidic pH and a selective complexation of ATP by L^2 at basic pH. Preferential ATP interaction by receptor L^2 at basic pH can be attributed to the higher basicity of L^2 when compared with L^3, whereas when both receptors are protonated the stronger interaction of L^3 might be due to the closer proximity between polyammonium groups. Ternary diagrams for the L^2–H^+–ATP, phosphate system allow one to determine pH ranges of selective complexation of L^2 in an equimolar mixture of ATP and phosphate. They show the preferential co-ordination of L^2 towards ATP at basic pH and a selective complexation of phosphate at acidic pH. Similar results are obtained for the ternary L^3–H^+–ATP, phosphate system.

In conclusion, larger formation stability constants with phosphate or ATP are obtained with receptors containing more amino groups. By comparison between receptors having the same number of basic centres (for instance L^2 and L^3), larger stability constants are found for the receptor having closer amino groups. An enhancement of the formation stability constants is found in dioxane–water mixtures when compared with those obtained in water.

Table 5 Experimental and calculated electrochemical shift from acidic to basic pH for receptors L^1, L^2, L^3, L^4 and L^5

Ligand	$(\Delta E_{1/2})_{calc.}$ [a]	$(\Delta E_{1/2})_{exp.}$ [b]
L^1	275	290
L^2	330	310
L^3	380	360
L^4	85	80
L^5	120	140

[a] From eqn. (2). [b] From electrochemical data.

Electrochemical behaviour

The shift of the redox potential of the ferrocenyl groups as a function of the pH in the presence of phosphate and ATP has been monitored in water for L^1, L^2 and L^3 and in the presence of phosphate and sulfate in 1,4-dioxane–water (70 : 30 v/v) for L^4 and L^5. One of the most promising applications of redox-functionalised molecules is the incorporation in amperometric sensing devices of certain receptors showing a large and selective electrochemical shift against target substrates.

As already observed in related systems there is a steady anodic shift of the redox potential of the ferrocenyl groups from basic to acidic pH. The difference between the oxidation potential at basic and acidic pH has been measured for all the receptors and is shown in Table 5. From an electrochemical viewpoint polyammonium species are more difficult to be oxidised than the unprotonated receptor because there is extra electrical work related with the approach to a positively charged electrode of positively charged species. It has recently been reported[50] that in systems where there is no electronic communication between protonated groups and the ferrocene moiety the electrochemical shift due to the protonation of amines can theoretically be calculated by taking into account the free energy associated with the electrostatic repulsion between the ferrocenium cation and the ammonium groups. Following this approach eqn. (2) can be deduced with redox

$$\Delta E = \frac{1}{jn}\left[\frac{14398}{\varepsilon}\sum_j\sum_i\frac{1}{r_{ji}} + \left(\frac{2\times10^6}{\varepsilon^2}+1051\right)\sum_j\sum_i\frac{1}{r_{ji}^2}\right] \quad (2)$$

groups (j) and number of electrons (n). This equation allows prediction of the maximum electrochemical shift in ferrocene-functionalised receptors due to protonation processes. The only parameter to be determined is the distance between the ferrocene (iron atom) and all the ammonium groups, and the relative permittivity of the medium (ε can approximately be calculated for a mixture of solvents as $\Sigma x_i\varepsilon_i$, where x_i = molar fraction of the solvent i and ε_i = permittivity of solvent i). In case a crystal structure is not available, determination of the r_{ji}

Table 6 Cathodic electrochemical shifts of L^1, L^2 and L^3 in the presence of ATP and phosphate in water (25 °C, 0.1 mol dm^{-3} KNO_3) and cathodic electrochemical shifts of L^4 and L^5 in the presence of phosphate and sulfate in dioxane–water (70 : 30 v/v)

Ligand	Phosphate (pH)	ATP (pH)	Sulfate(pH)
L^1	30[a] (7–8)	40 (7–8)	
L^2	34 (7–8)	30 (7–8)	
L^3	25 (8–9)	30 (7–8)	
L^4	15 (6–7)		15 (6–7)
L^5	10 (6–7)		<5

[a] In mV.

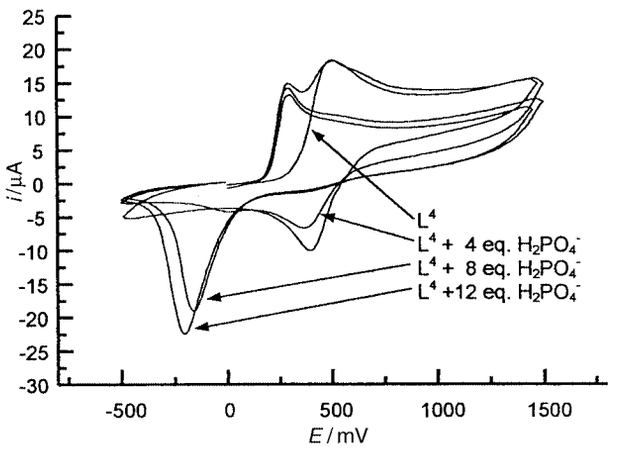


Fig. 6 Cyclic voltammogram (100 mV s^{-1}) of L^4 in the presence of successive amounts of $H_2PO_4^-$ in acetonitrile, 0.1 mol dm^{-3} tetrabutylammonium perchlorate.

distances by a modelling program is usually sufficient. The results compare well with those experimentally obtained (see Table 5).

Electrochemical studies of L^1, L^2 and L^3 as a function of the pH in water in the presence of phosphate and ATP showed maximum electrochemical shifts of *ca.* 30–40 mV at neutral pH (see Table 6). We have also recently reported[51] poor electrochemical shifts of *ca.* 30–40 mV at neutral pH against phosphate using related ferrocene-functionalised tetraamines. However, whereas in the present work maximum cathodic shifts in the presence of ATP were found to be less than 30 mV, for other ferrocene-functionalised tetraamines ATP has been reported cathodically to shift the oxidation potential of the ferrocenyl groups up to *ca.* 100 mV.[51]

The electrochemical behaviour of L^4 and L^5 as a function of the pH in 1,4-dioxane–water (70 : 30 v/v) mixtures has been studied in the presence of phosphate and sulfate (ATP is not soluble in this mixture). Results are shown in Table 6. For these receptors neither the presence of sulfate or phosphate modifies significantly the oxidation potential of the ferrocenyl groups (the largest electrochemical shift is less than *ca.* 20 mV). Despite the cyclic nature of L^4 the electrochemical response against anions is very poor. Such a poor response has also been observed for the N-ferrocene-functionalised derivative of the polyazacycloalkane 1,4,7,10,13,16-hexaazacyclooctadecane.[45]

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 to that observed in water due to the lower relative permittivity of the molecule in this medium. In order to study how the change of the relative permittivity affects the electrochemical response against anions, we have also studied the electrochemical shift

Table 7 Voltammetric data for the free L^4, L^5 receptors and for L^4, L^5 in the presence of HSO_4^- and $H_2PO_4^-$ in dry acetonitrile, in 0.1 mol dm^{-3} tetrabutylammonium perchlorate

System	E_{pa}/V	E_{pc}/V	$E_{1/2}$/V
L^4	500	400	450
L^4 + 10 equivalents HSO_4^-	500	170	
L^4 + 10 equivalents $H_2PO_4^-$	300	−200	
L^5	480	370	425
L^5 + 10 equivalents HSO_4^-	480	130	
L^5 + 10 equivalents $H_2PO_4^-$	395	0	

E_{pa} and E_{pc} are the oxidation and reduction wave potential; $E_{1/2} = (E_{pa} + E_{pc})/2$; $\Delta E_{ac} = (E_{pa} - E_{pc})$.

induced by HSO_4^- and $H_2PO_4^-$ in the receptors L^4 and L^5 in acetonitrile solutions (due to its insolubility ATP could not be studied). Fig. 6 shows the changes in the voltammetric wave of receptor L^4 after progressive addition of $H_2PO_4^-$. L^4 shows a typical reversible oxidation wave at *ca.* 500 mV. Addition of 4 equivalents of $H_2PO_4^-$ produces the appearance of a new oxidation peak at *ca.* 300 mV. Successive addition of this anion results in the extinction of the former oxidation wave of the free receptor and the appearance of a cathodically shifted irreversible wave (electrochemical–chemical (EC) process). The observed behaviour can be explained taking into account that both the free receptor and its oxidised form can bind the $H_2PO_4^-$ anion. The cathodic shift of the anodic peak (E_{pa}) from 500 to 300 mV is due to the formation of the complex $[L^4H_2PO_4]^-$. This complex has a negative charge and its anionic nature makes it easier to oxidise when compared to the free neutral receptor. The new cathodic peak (E_{pc}) at −200 mV after addition of $H_2PO_4^-$ (600 mV shifted from the former E_{pc} peak of the free receptor at 400 mV) is assigned to the extra strong interaction between the oxidised ferrocenium groups and the phosphate anion. A similar behaviour is observed when increasing quantities of $H_2PO_4^-$ are added to acetonitrile solutions of L^5 (see Table 7).

We have also studied the changes in the oxidation wave profile of L^4 in the presence of the HSO_4^- anion. Increasing amounts of HSO_4^- (up to 12 equivalents) do not produce any significant shift in the anodic peak of the ferrocenyl groups although, as for phosphate, an EC profile was observed after addition of four equivalents. The E_{pc} peak in the presence of sulfate appears at 170 mV (230 mV shifted from that of the free receptor) whereas that for phosphate was found near −200 mV. The results suggest that there is a selective sensing response for phosphate over sulfate. This contrasts with what was observed for the analogous electroactive-functionalised receptor 1,15-diferrocenyl-2,5,8,11,14-pentaazapentadecane (a pentaaza open-chain polyamine functionalised with two ferrocenyl groups) for which both phosphate and sulfate produced similar changes in the voltammogram of the ferrocenyl groups.[52] L^5 shows a similar behaviour in the presence of sulfate to that found for L^4 (see Table 7).

Acknowledgements

We should like to thank the Dirección General de Investigación Científica y Técnica (proyecto PB98-1430-C02-02 and 1FD97-0508-C03-01 and AMB99-0504.C02-01) for support. We would also like to thank EPSRC for a studentship to J. C. and for use of the mass spectrometry service at the University of Wales, Swansea.

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