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Coordination Chemistry Reviews
185–186 (1999) 3–36

COORDINATION
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Mechanisms of electrochemical recognition of cations, anions and neutral guest species by redox-active receptor molecules

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Received 26 October 1998

Contents

Abstract

This short review highlights the mechanisms involved in electrochemically sensing cationic, anionic and neutral guest species by redox-active receptors and is an update to a previously published review article (P.D. Beer, P.A. Gale, Z. Chen, Adv. Phys. Org. Chem. 31 (1998) 1). Mechanisms of redox–complexation coupling are discussed together with recent examples of redox-responsive molecular receptors from the literature that illustrate them. © 1999 Elsevier Science S.A. All rights reserved.

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PII: S0010-8545(98)00246-X

Keywords: Electrochemistry; Molecular recognition; Sensors; Supramolecular chemistry

1. Introduction

The study of the electrochemical properties of supramolecular systems is an area of intense current interest [1]. A subset of this field of study is the production of redox-active molecular receptors capable of sensing charged or neutral substrates and reporting their presence by means of an electrochemical response [2,3]. The receptors discussed in this review consist of a guest binding site in close proximity to a redox active moiety (Fig. 1). The electrochemical recognition of a guest by such a receptor requires that the guest binding site and the redox active group can communicate [4,5]. Evidently, selective binding of a particular guest species coupled with an electrochemical response is of paramount importance for future potential prototypes of new amperometric molecular sensory devices [6]. This review highlights the mechanisms involved in communicating the binding event to the redox-active centre of the receptor. It is an update to a previous review article [7] and covers the period 1996–to date of submission.

2. Coupled reaction systems

The stability constant K of a host/guest (1:1) complex is defined by the equilibrium:

$$\mathrm{H} + \mathrm{G} \underset{k_d}{\overset{k_c}{\rightleftarrows}} \mathrm{HG}$$

$$\mathrm{K} = \frac{k_c}{k_d} = \frac{[\mathrm{HG}]}{[\mathrm{G}][\mathrm{H}]} \quad (1)$$

where H, G and HG represent the host, guest and complex species.

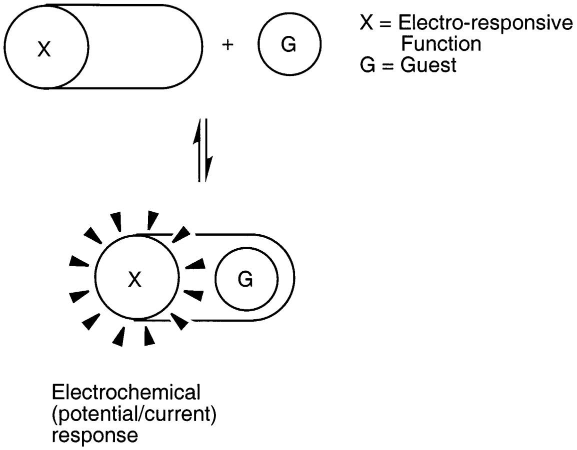


Fig. 1. An electrochemical response is generated by the receptor upon guest binding.

$$\begin{tikzcd}
H_{ox} \arrow[r, shift left, "+e"] \arrow[d, shift right, "+G"'] & H_{red} \arrow[l, shift left, "E^{\circ}_{H}"] \arrow[d, shift right, "+G"'] \\
HG_{ox} \arrow[u, shift right, "K_{ox}"'] \arrow[r, shift left, "+e"] & HG_{red} \arrow[l, shift left, "E^{\circ}_{HG}"] \arrow[u, shift right, "K_{red}"']
\end{tikzcd}$$

Scheme 1. The scheme of one square for guest binding and electron transfer.

Studies in the area of electrochemical molecular recognition deal with bifunctional receptor molecules that contain not only binding sites but also redox-active centres whose electron transfer reaction is coupled to the receptor's complexation. Such systems can be described by the scheme of one square as shown below (Scheme 1).

In this scheme, H, G and HG in normal or subscript positions, represent the host, guest and complex species, respectively; subscripts ox and red indicate that the corresponding molecules or parameters are in oxidised and reduced states; E° is the formal potential of the electron transfer reaction and K is the stability constant. According to thermodynamics, there are four relationships linking the concentrations of the four molecules at the four corners of the square. These are two Nernst equations for the upper (Eq. (2)) and lower (Eq. (3)) electron transfer reactions,

$$(E - E^{\circ}_{\mathrm{H}})nF/RT = \ln([\mathrm{H}_{\mathrm{ox}}]/[\mathrm{H}_{\mathrm{red}}]) \tag{2}$$

$$(E - E^{\circ}_{\mathrm{HG}})nF/RT = \ln([\mathrm{HG}_{\mathrm{ox}}]/[\mathrm{HG}_{\mathrm{red}}]) \tag{3}$$

Combining Eqs. (2) and (3):

$$(E^{\circ}_{\mathrm{H}} - E^{\circ}_{\mathrm{HG}})nF/RT = \ln([\mathrm{HG}_{\mathrm{ox}}][\mathrm{H}_{\mathrm{red}}]/[\mathrm{HG}_{\mathrm{red}}][\mathrm{H}_{\mathrm{ox}}])$$

$$(E^{\circ}_{\mathrm{H}} - E^{\circ}_{\mathrm{HG}})nF/RT = \ln([\mathrm{HG}_{\mathrm{ox}}][\mathrm{H}_{\mathrm{red}}][\mathrm{G}]/[\mathrm{HG}_{\mathrm{red}}][\mathrm{H}_{\mathrm{ox}}][\mathrm{G}])$$

$$(E^{\circ}_{\mathrm{H}} - E^{\circ}_{\mathrm{HG}})nF/RT = \ln\{([\mathrm{HG}_{\mathrm{ox}}]/[\mathrm{G}][\mathrm{H}_{\mathrm{ox}}])/([\mathrm{HG}_{\mathrm{red}}]/[\mathrm{G}][\mathrm{H}_{\mathrm{red}}])\}$$

The two complexation equilibrium equations for the left (Eq. (4)) and right (Eq. (5)) complexation/decomplexation equilibria are:

$$K_{\mathrm{ox}} = [\mathrm{HG}_{\mathrm{ox}}]/[\mathrm{G}][\mathrm{H}_{\mathrm{ox}}] \tag{4}$$

$$K_{\mathrm{red}} = [\mathrm{HG}_{\mathrm{red}}]/[\mathrm{G}][\mathrm{H}_{\mathrm{red}}] \tag{5}$$

Therefore:

$$(E^{\circ}_{\mathrm{H}} - E^{\circ}_{\mathrm{HG}})nF/RT = \ln(K_{\mathrm{ox}}/K_{\mathrm{red}}) \tag{6}$$

Eq. (6) links, in a simple way, the thermodynamically important stability constants K_{ox} and K_{red} of a complex in different oxidation states with experimentally measurable redox potentials E_{H} and E_{HG}. Therefore, it enables an easy way to obtain the ratio of K_{ox}/K_{red} which is a theoretically useful parameter known as the binding enhancement factor (BEF). We have proposed [7] that a better description for this ratio would be the reaction coupling efficiency (RCE) as binding by so-called molecular switches may be decreased or increased, depending upon the particular system involved. Eq. (5) also allows the calculation of K_{ox} if K_{red} is known or vice versa.

Receptors designed to electrochemically recognise guest molecules must couple the complexation process to the redox reaction, i.e. the two reactions must mutually influence each other. Electron insertion (reduction) or withdrawal (oxidation) from a host molecule will change the stability constant of the complex formed, leading to a change in the ratio of K_{ox}/K_{red}. Eq. (6) predicts that this change in stability constant will cause a change in the host's redox potential. The magnitude and the direction of the potential change will depend primarily on the reaction coupling mechanism and the properties of the complexed guest molecule. The variations can be measured for example, by voltammetric means.

3. Pathways for coupling electrochemical/complexation reactions

The electrochemical molecular recognition process should result in a large shift of the redox potential of the host species. The minimum magnitude of a potential shift is gauged by experimental error, which for most voltammetric techniques is ca. ± 5 mV. According to Eq. (6), the potential shift is determined by the ratio of K_{ox}/K_{red}. This reflects the influence of the redox reaction upon complexation, in other words, the RCE. So far, the coupling has been mainly realised through one or a combination of the following five pathways [7] (Fig. 2):

1. Through space electrostatic interaction between the redox centre(s) and the complexed guest molecule [8];
2. Through bond communication provided typically by conjugated chemical bond linkage between the redox centre(s) and the binding cavity [9];
3. Additional direct co-ordination bond formation between the redox centre and the complexed guest molecule [10];
4. Conformational induced perturbation of the redox centre(s) caused by the complexation of a guest molecule [11];
5. Interference by the guest species in communication between two redox-active centres [12].

4. Electrochemical recognition of cations

Redox-active receptors for cations maybe either oxidizable (and hence form less stable complexes with cations), e.g. ferrocene containing receptors, or reducible (and hence form more stable complexes with cations), e.g. quinone, anthraquinone and nitroaromatic containing species. Cyclic voltammetry (CV), square wave voltammetry (SWV) [13] and rotating disk techniques are widely used to monitor perturbations in the electrochemical behaviour of redox-active receptor species. In all cases we should expect to see an anodic shift of the redox-process being observed as the positively charged cation–receptor complex will be harder to oxidize (or more easy to reduce) than the neutral receptor alone.

4.1. Ferrocene based receptors for metal cations

The use of ferrocene modified crown ethers as redox-active ionophores for metal cations has been explored by a number of research groups (see our previous review) [7]. Grossel and co-workers have re-examined the coordination properties of a number of ferrocene (and ruthenocene) aza-crown ether species (e.g. compound **1**) and discovered, by careful analysis of ^{13}C-NMR binding studies, a possible π-interaction between the bound metal ion and the metallocene ring system (Scheme 2) [14]. There may therefore be a direct coordination pathway possible in this type of receptor as the metal cation maybe directly coordinated to the redox active metallocene.

Plenio and co-workers have specialized in producing systems where donor atoms are attached directly to the Cp ring of ferocene or cobaltocene organometallic fragments. This allows a through bond as well as a through space coupling of the electrochemical and complexation processes. This is illustrated by the large electro-

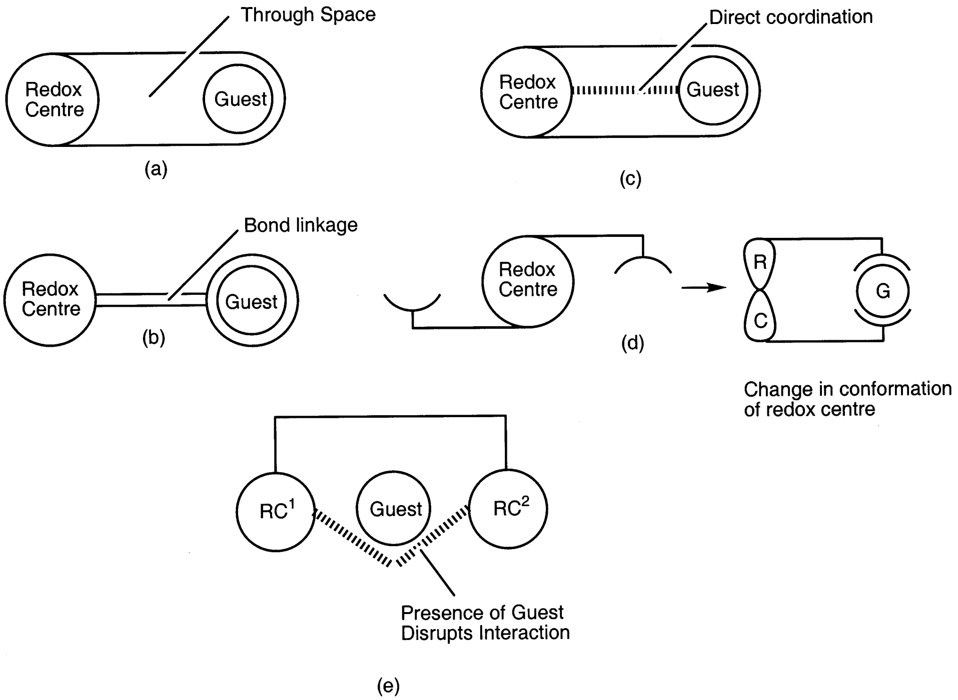
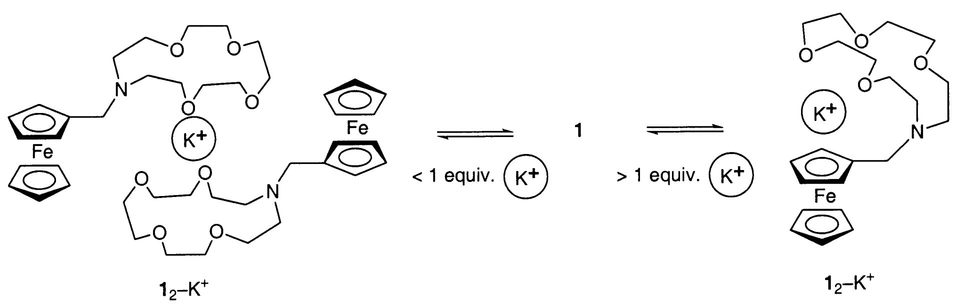


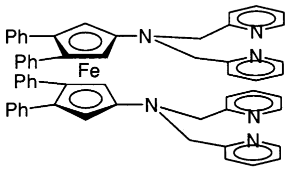
Fig. 2. The mechanisms for coupling electrochemical and complexation reactions.



Scheme 2. A π-cation interaction may be involved in potassium binding by **1** at > one equivalents of K^+.

chemical shifts of compound **2** (that contains nitrogen atoms directly attached to a ferrocene cyclopentadienyl ring) in the presence of transition metal cations. This receptor produced very large cathodic shifts when coordinated to Zn^{2+} ($\Delta E_{1/2} =$ 330 mV for one equivalent of Zn^{2+} and $\Delta E_{1/2} = 720$ mV for two equivalents of Zn^{2+}) and Co^{2+} ($\Delta E_{1/2} = 380$ mV for one equivalent of Co^{2+} and $\Delta E_{1/2} = 760$ mV for two equivalents of Co^{2+}) [15].

A similar system with aza-crown ethers attached directly to a cobaltocene moiety produced shifts of up to 190 mV in the presence of Li^+ cations (compound **3**) [16]. The properties of analogous molecules with larger crown ether ring systems (**4** and **5**) were also reported.



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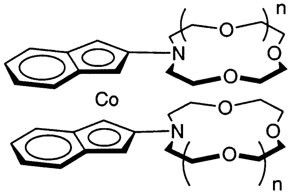


3 n = 1
4 n = 2
5 n = 3

Plenio and co-workers have also produced a series of ferrocene cryptands **6**–**8** that maximize coupling between the bound metal ion and the metallocene centre by attaching oxygen donor atoms directly to the ferrocene cyclopentadienyl ring [17]. Syntheses involving hydroxyferrocenes are complicated by virtue of these species being unstable. Plenio therefore used ferrocenyl silyl ethers as stable synthetic intermediates, thus allowing the oxaferrocene cryptands to be isolated in high yields (Scheme 3).

CV studies of the three receptors were conducted in acetonitrile in the absence and presence of alkali and alkaline earth metal cations. The results are presented in Table 1. Large anodic shifts of the ferrocene/ferrocenium redox couple were observed on addition of metal cations (the largest shift of 380 mV was observed on addition of Ca^{2+} to receptor **6**). The shifts with alkali metal cations followed two trends: (a) the larger the cavity (the more donor atoms present) the lower the shift; and (b) metal ions that are complementary to the size of the cavity produce the

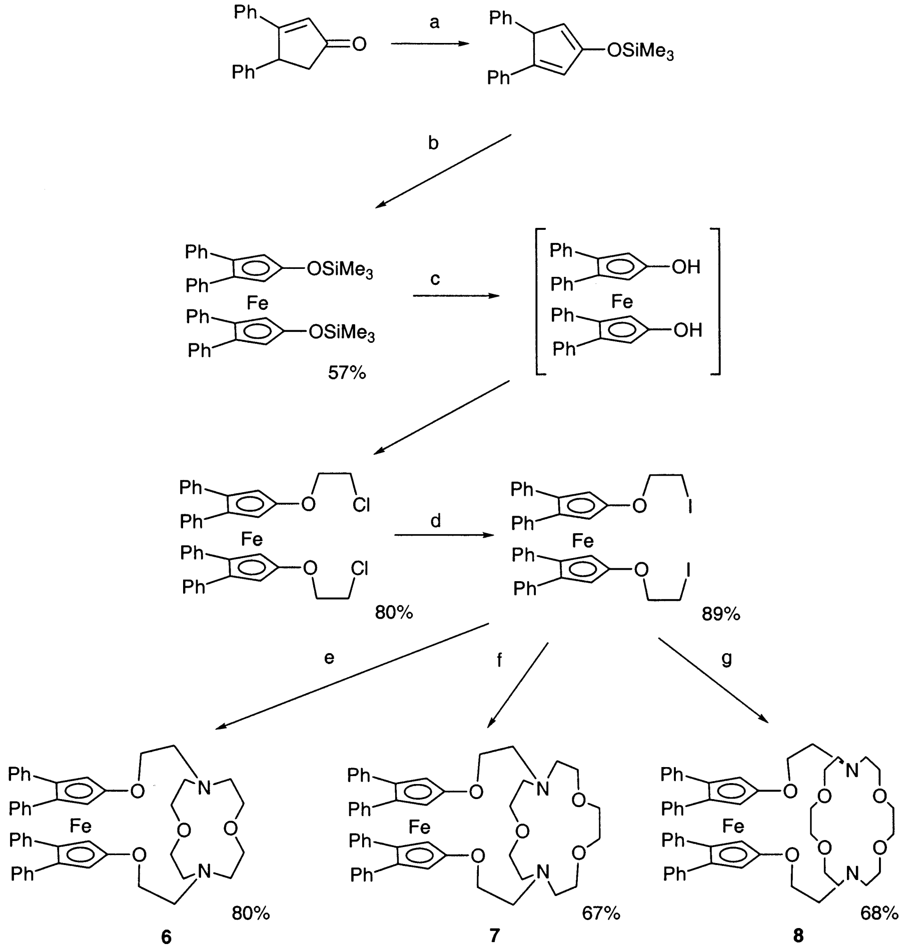
Table 1
Summary of the redox potentials of the ferrocene cryptands **6**, **7** and **8** and their different alkali and alkaline earth metal ion complexes[a]

Metal	(None)	Li^+	Na^+	K^+	Rb^+	Cs^+	Ca^{2+}	Sr^{2+}	Ba^{2+}
6									
$E_{1/2}$ (V)	+0.290	+0.450	+0.505	+0.390	+0.390	+0.385	+0.670	+0.650	+0.595
$\Delta E_{1/2}$ (mV)	+160	+215	+100	+100	+95	+380	+360	+305	
7									
$E_{1/2}$ (V)	+0.285	+0.385	+0.465	+0.455	+0.430	+0.375	+0.605	+0.565	+0.585
$\Delta E_{1/2}$ (mV)		+100	+180	+170	+145	+90	+320	+280	+300
8									
$E_{1/2}$ (V)	+0.285	+0.365	+0.365	+0.410	+0.435	+0.400	+0.445	+0.480	+0.550
$\Delta E_{1/2}$ (mV)		+80	+80	+125	+150	+115	+160	+195	+265

[a] All CVs were recorded in acetonitrile at ambient temperatures using group 1 and 2 triflates or perchlorates. A three electrode configuration was employed. The working electrode was a Pt disk (diameter 1 mm) sealed in soft glass with a Pt wire counter electrode. The pseudoreference was an Ag wire. Potentials were calibrated internally against the formal potential of cobaltocenium perchlorate (−0.94 V vs. Ag | AgCl) or octamethylferrocene (−0.025 V vs. Ag | AgCl). Solutions were ca. 2×10^{-4} M in compound.

largest anodic shift $\Delta E_{1/2}$. These trends can be explained by the decreasing relative importance of the Cp ring bound oxygen atoms as the overall number of oxygen atoms increases. This also causes an increase in the iron–metal distance. These donor atoms are most important when the bound cation is complementary to the size of the cavity.

Plenio has recently used compound **2** in an artificial regulatory system consisting of two coupled molecular switches that can regulate sodium ion concentrations [18].



a) $CF_3SO_3SiMe_3$, Et_3N, petroleum ether; b) n-BuLi, $FeCl_2$, THF;
c) CH_3CN +10% H_2O, Na_2CO_3;ClC_2H_4(tosylate), reflux;
d) NaI, acetone, reflux, e) diaza-12-crown-4, Na_2CO_3, CH_3CN, reflux
e) diaza-15-crown-5, Na_2CO_3, CH_3CN, reflux
f) diaza-18-crown-6, Na_2CO_3, CH_3CN, reflux

Scheme 3. Syntheses of compounds **6**, **7** and **8**.

Table 2
CV data for compounds **9–11**

Ligand/ metal	$E_{1/2\ \mathrm{free}}$	$E_{1/2\ \mathrm{complex}}$	Min equivalents M^{2+} [a]	Max equivalents M^{2+} [b]	RCE ($K_{\mathrm{neutral}}/K_{\mathrm{ox}}$)
9/Ca	490	[c]	0.1	0.5	
9/Mg	490	720	0.1	3	3.8×10^5
10a/Ca	670	980	0.1	1	1.7×10^5
10a/Mg	670	1000	0.1	3	3.8×10^5
10b/Ca	680	1040	0.1	3	1.2×10^6
10b/Mg	680	1040	1	5	1.2×10^6
11/Ca	650	810	0.1	3	5.0×10^3
11/Mg	650	840	1	15	1.6×10^3

[a] Minimum equivalents of metal ClO_4^- required to produce a detectable second redox wave.

[b] Equivalents of metal required for complete disappearance of original redox wave.

[c] No new redox wave observed (waves anodically shifted). Experiments used the ligand (10^{-3} M) and n-Bu_4NClO_4 (0.1 M) in MeCN, vs. Ag | AgCl with a platinum working electrode. Sequential additions of aliquots of 0.1 or 0.5 equivalents of 10^{-2} M solutions of the appropriate metal salt in MeCN were monitored by CV.

Bryce and co-workers have reported that the nitrogen containing ferrocene derivatives **9–11** act as selective electrochemical sensors for Mg^{2+} and Ca^{2+} in acetonitrile solution via a through space mechanism.[19] Electrochemical data are presented in Table 2. The cyclic voltammogram of **9** in the absence and presence of 0.2 equivalents of $Mg(ClO_4)_2$ is shown in Fig. 3. After the addition of 0.2 equivalents of magnesium cations, two redox waves are observed corresponding to free and complexed receptor **9**. At this point the two oxidation processes have equal current suggesting that a 2:1 receptor–cation complex has formed in solution.

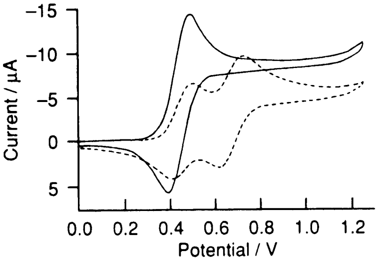
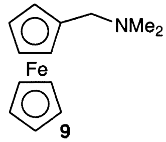


Fig. 3. CV of **9** in MeCN (continuous line) and after addition of $Mg(ClO_4)_2$ (· · ·, 0.2 equivalents). (Reproduced with permission from Chem. Commun. (1998) 677, Copyright 1998, The Royal Society of Chemistry.)

Remarkably, the addition of high concentrations of Li^+, Na^+, K^+, Cs^+, Ba^{2+}, and Ag^+ cations had no effect on the CVs of these receptors.



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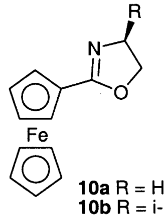
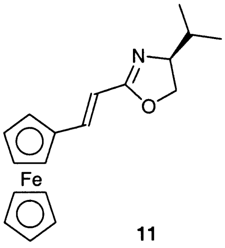


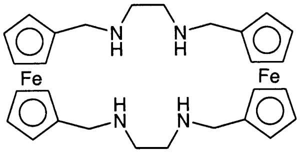
10a R = H
10b R = i-Pr



11

Recently a number of systems that are capable of sensing transition metals in aqueous environments have been reported [20,21]. These receptors consist of ferrocene signalling groups linked to binding sites containing polyamine functionalities. The perturbation caused by the presence of the transition metal in these systems (mediated by a through space mechanism) is pH dependent. Additionally, as these systems may also act as bases when protonated, they may be used to detect anions (see our previous review) [7].

Martínez-Máñez and co-workers have described a number of such systems. The electrochemical recognition of transition metal cations by a macrocyclic ferrocene receptor **12** has recently been described [22]. These researchers found that the electrochemical recognition ability of this ligand can be tuned by changing the pH in solution. The tuning can increase the response towards a particular metal cationic substrate (in this case Cu^{2+} and for an example of a mercury selective receptor see compound **14** below) or its presence can be masked. The maximum oxidation potential shift of these types of receptor may be predicted using an empirical expression taking account of the charge of the oxidized receptor, the charge of the substrate, the number of electrons transferred in the electrochemical process, the number of redox-active units, the distance between the redox-active groups and the substrate and the macroscopic relative permitivity of the medium [23].



12

For example receptor **13**, a ferrocene-functionalized polyazacycloalkane may be used to quantitatively detect Cu^{2+}, Zn^{2+}, and Cd^{2+} (as well as ATP) in aqueous solution [24]. Fig. 4a shows the variation of the oxidation potential of the systems **13**–H^+–M^{2+} at different pHs (this data was obtained in THF–water 70:30 v/v with a ligand-to-metal ratio of 1:1). The oxidation potential of **13** shifts anodically as the pH is lowered, as a result of successive protonations of the amino groups. For metal-to-ligand ratios < 1, curves between the free curve of **13** and the 1:1 complex

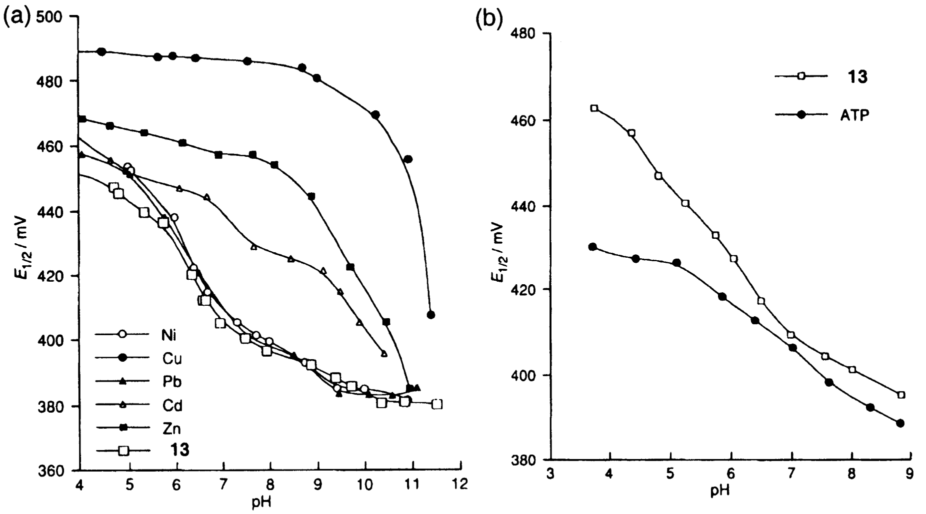
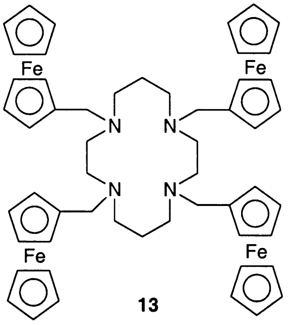


Fig. 4. (a) A plot of $E_{1/2}$ vs. pH for **13**–H$^+$and **13**–H$^+$–M^{2+} (M^{2+} = Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}) and (b) a plot of $E_{1/2}$ vs. pH for **13**–H$^+$and **13**–H$^+$–ATP. (Reproduced with permission from Chem. Commun. (**1997**) 887, Copyright 1998, The Royal Society of Chemistry.)

curve are obtained. This allows the concentration of metal ions in solution to be obtained provided the concentration of receptor in solution is known.



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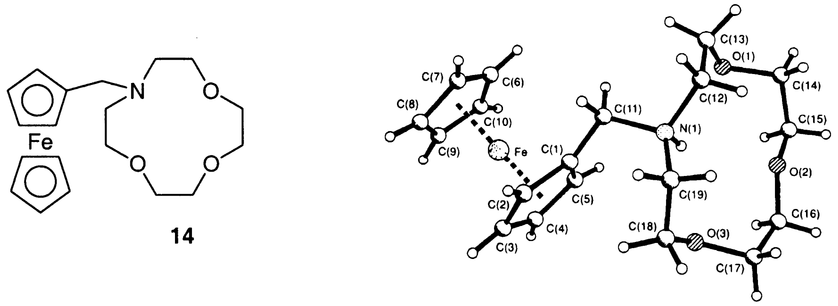


Fig. 5. The structure of compound **14** and crystal structure of the **14**–H$^+$cation. (Reproduced with permission from Chem. Commun. (**1998**) 837, Copyright 1998, The Royal Society of Chemistry.)

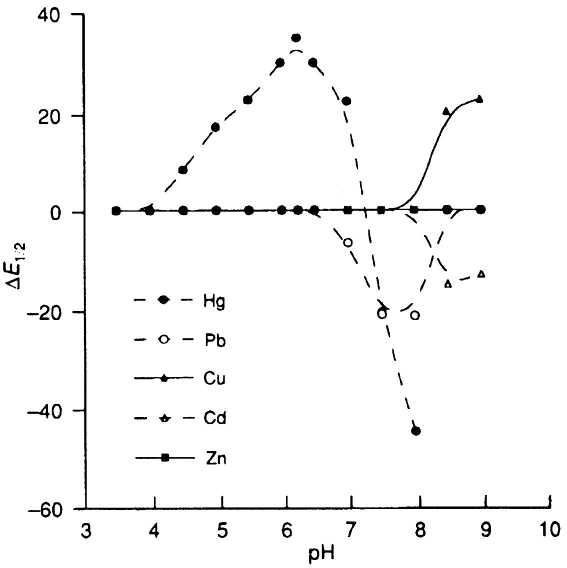
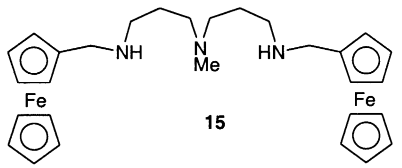


Fig. 6. A plot of $\Delta E_{1/2}$ vs. pH as a function of the pH for **14**–H^+–M^{2+} (M^{2+} = Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, and Hg^{2+}). (Reproduced with permission from Chem. Commun. (**1998**) 837, Copyright 1998, The Royal Society of Chemistry.)

Compound **13** when mono-protonated also acts as a sensor for ATP anions. Fig. 3b shows the variation of oxidation potential of **13**–$H^+$and **13**–H^+–ATP with pH. Thus compound **13** may also be used to quantitatively determine ATP concentrations in aqueous solution.

In a separate communication Martínez-Máñez reported that the ferrocene aza-oxa crown derivative **14** (Fig. 5) may be used to electrochemically recognise mercury (via a through space mechanism) [25]. 1,4,5-Trioxa-10-azacyclododecane (which is a mercury selective macrocycl) was functionalized with a ferrocenyl group by reaction of the macrocycle with (ferrocenylmethyl)trimethylammonium iodide in acetonitrile. As the macrocycle is selective for mercury, the formation of **14**–Hg^{2+} is able to occur at a lower pH than that for other transition metal ions. Indeed at pHs around 5 other transition metals are unable to form complexes with **14** due to protonation of the macrocycle. The mercury complex does form at pH 5, therefore, by studying the change in oxidation potential with pH, the presence of mercury ions may be detected in solution (Fig. 6).

Beer and Smith have produced a series of acyclic ferrocene receptor species (**15**–**18**) and studied the effects of adding transition metal cations (as hydrated perchlorate or tetrafluoroborate salts) to electrochemical solutions of the receptors [26]. The metal ions can either coordinate to the receptors, or alternatively act as acids and protonate them. Protonation will also cause a shift in the ferrocene oxidation potential (addition of HBF_4 caused a shift of ca. 160 mV with each receptor). It was found that receptors that are inefficient (e.g. **17** with a large donor bite angle) are more likely to be protonated rather than coordinate to the transition metal cations (i.e. a large shift of approximately 160 mV will be observed). The results are presented in Table 3. Receptors **16** and **17** are protonated on addition of any of the metal cations whereas receptor **18** complexes transition metal cations with anodic shifts up to 115 mV with Ni(II). Receptor **18** is capable of coordinating to the transition metal via the pyridine nitrogen atom (that is not present in receptor **17**).



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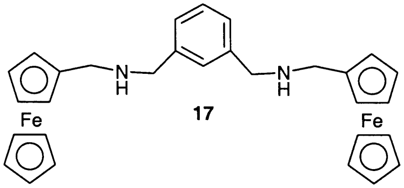

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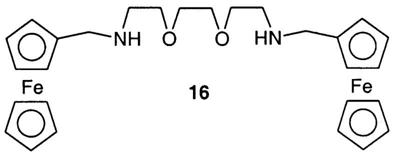

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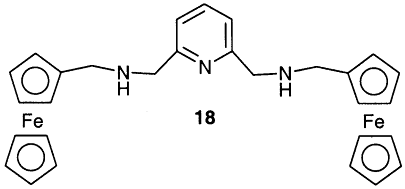


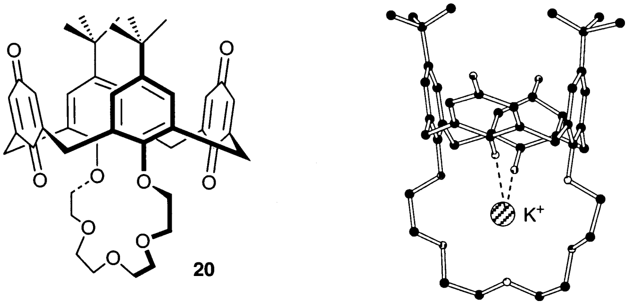
18

The detection of two different cations simultaneously by a single redox-active receptor is a difficult challenge. Beer and co-workers found receptor **19** which contains two metal binding sites produces could be used to sense the presence of barium, magnesium, or a mixture of barium and magnesium via a through space interaction [27]. Novel three peak voltammetric features are observed for **19** in the presence of both Mg^{2+} and Ba^{2+}, which correspond to the three complexes

Table 3
Electrochemical shifts (mV) of the ferrocene redox couple in acetonitrile on the addition of metal ion salts as hydrated perchlorates/tetrafluoroborates (n.i. = not investigated)[a]

		Metal salt (Δ*E* mV)				
Compound	Free $E_{1/2}$(V)	Ni(II)	Cu(II)	Zn(II)	Ca(II)	Pb(II)
15	0.05*	58^c	98^c	162^p	n.i.	n.i.
16	0.027	73^c	160^p	168^p	172^p	165^p
17	0.040	175^p	169^p	n.i.	160^p	n.i.
18	0.030	115^c	105^c	75^c	158^p	n.i.

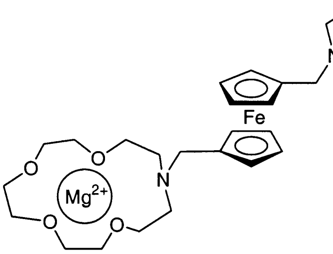
[a] In each case the electrochemical response corresponds to either protonation (p) or complexation of the metal ion (c). * Broad oxidation peak. All $E_{1/2}$ values (quoted for the ferrocene wave) are relative to $Ag^+ \mid Ag$ in MeCN and are accurate to ±5 mV.



20

Fig. 7. The structure of compound **20** together with the crystal structure of the potassium complex (counter perchlorate anion not shown). Quinone–potassium interactions are shown by dotted lines.

19–$2Ba^{2+}$, **19**–$2Mg^{2+}$ and **19a**–Ba^{2+}–Mg^{2+} anodically shifted from the free ligand by 150, 395 and 275 mV, respectively (see our previous review [7]).



19–Ba^{2+}–Mg^{2+}

Table 4
Reduction potentials of **20** and the anodic shifts in the presence of one or two equivalents of different cationic species

Solution	E_{pc} (V) of each redox couple (vs. Ag | Ag^+)[a]	
$E_{1/2}$ (free, V)	−1.155	−1.930
ΔE (K^+, mV)[b]	210	250
ΔE (Na^+, mV)[b]	255	290
ΔE (Ba^{2+}, mV)[b]	555	[d]
ΔE (NH_4^+, mV)[c]	405	[d]
ΔE (n-$BuNH_3^+$, mV)[c]	355	[d]

[a] Obtained by both cyclic (100 mV s^{-1}) and square wave (10 Hz, Osteryoung-type) voltammetry in acetonitrile solution containing 0.1 M n-Bu_4NBF_4 as supporting electrolyte. Solutions were ca. 1×10^{-3} M in compound with reference to a Ag | Ag^+ electrode (330 ± 10 mV vs. SCE) at 21 ± 1°C.

[b] Anodic shift of the reduction waves of **20** in the presence of 1.0 equivalent of the respective cationic species added as their perchlorate or hexafluorophosphate salts.

[c] Anodic shift in the presence of 2.0 equivalents of the respective cations.

[d] The second reduction wave of **20** became obscure or disappeared in the presence of more than one equivalents of the respective cations.

4.2. Other cation sensors

The incorporation of quinone groups into macrocyclic receptors can produce redox-active species capable of very large shifts in redox-potential. This is due to the direct coordination of the quinone moiety to the added cation. One such receptor **20** incorporates quinone groups into a calixarene skeleton that is bridged by a crown-ether like polyglycol strand. The crystal structure of the potassium perchlorate complex of this receptor is shown in Fig. 7. In this case the two quinone groups are coordinated directly to the added metal cation which is also bound to the phenolic groups at the lower rim of the calixarene and to the crown ether oxygen atoms. The electrochemical responses of **20** upon addition of cations are shown in Table 4. Particularly notable is the anodic shift of 555 mV observed on addition of barium cations (which to the best of our knowledge is the largest shift so far observed for any redox-active receptor on addition of alkaline earth metal cations) [10].

Recently Shephard, Johnson, and co-workers have reported the synthesis and coordination properties of redox-active ruthenium cluster crown compounds that are capable of electrochemically detecting Na^+ and $NH_4{}^+$ cations [28] Benzo-15-crown-5 and benzo-18-crown-6 were reacted with $[Ru_6C(CO)_{17}]$ causing displacement of CO groups and coordination of the ruthenium metal to the aromatic ring present in the crown ethers, producing compounds **21** $[Ru_6C(CO)_{14}(h^6$-benzo-15-crown-5$]$ and **22** $[Ru_6C(CO)_{14}(h^6$-benzo-18-crown-6$]$. The crystal structure of the ammonium complex of **22** is shown in Fig. 8.

The electrochemical properties of **22** were studied by CV in dichloromethane solution with a Ag|AgCl reference electrode. A reduction peak was observed at -0.91 V with a re-oxidation process at -0.17 V. Addition of sodium or ammonium ions caused a new reduction wave to evolve at ca. -0.65 V, for both Na^+ and NH_4^+ (Fig. 9) indicating that the binding and complexation process are coupled together presumably by a mixture of through bond and through space interactions.

5. Electrochemical recognition of anions

The electrochemical detection of anionic species is a particular challenge [29]. Anion binding has generally proved to be more challenging (with respect to cations) due to their lower charge to radius ratio, pH sensitivity and range of geometries. Chemically, anions are utilised in many chemical reactions acting as nucleophiles (CN^-), bases (^-OR) and redox active centres ($S_2O_8{}^{2-}$). The environmental impact of anionic pollutants such as excess nitrates from agricultural fertilisers leads to eutrophication of rivers. Surprisingly then, specific ligands that have the capability of optically and/or electrochemically detecting anions are still rare. Electrochemical receptors for anions are expected to show cathodic shifts in their redox-process when complexed to an anion as they are either easier to oxidize or harder to reduce than the free redox-active receptor.

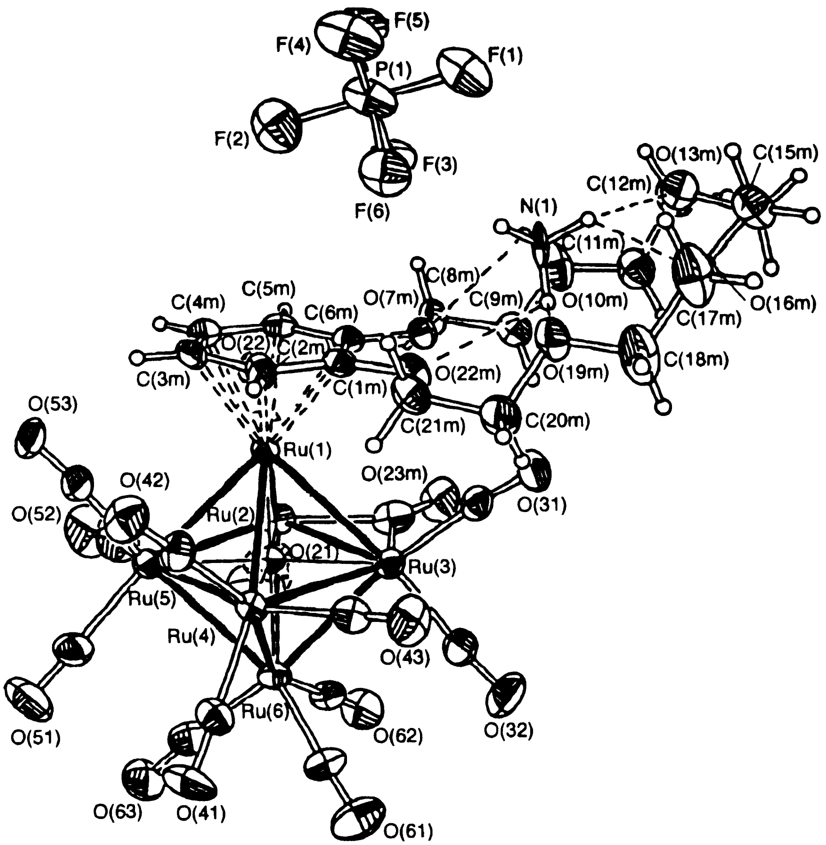


Fig. 8. The solid state molecular structure of **22** · NH_4^+ (Reproduced with permission from J. Chem. Soc. Dalton Trans. (**1998**) 2289, Copyright 1998, The Royal Society of Chemistry.)

Combining amide hydrogen bond donor groups with redox-active moieties [29], Beer and co-workers synthesized a series of atropisomers of 5, 10, 15, 20-tetrakis-(*o*-ferrocenylcarbonylaminophenyl-subsituted) zinc metalloporphyrins and found that complexes are formed with halide, nitrate and hydrogen sulfate anions with selectivity trends dependent upon the particular atropisomer. Compounds **23** (α, α, α, α-), **24** (α, α, α, β-), **25** (α, α, β, β-) and **26** (α, β, α, β-) were prepared and the stability constants found with Cl^-, Br^-, HSO_4^- and NO_3^- using ^{1}H-NMR titration techniques in dichloromethane-d_2. The receptors were found to be selective for halides over other anions apart from **24** which is selective for NO_3^- over Cl^-. Cathodic shifts of both porphyrin and ferrocene centred oxidations were observed upon addition of anions to solutions of the receptors in dichloromethane/acetonitrile. The shifts are presumably mediated via a combination of through bond and through space interactions and are of up to 175 mV for the porphyrin based oxidation of receptor **25** on addition of HSO_4^-.

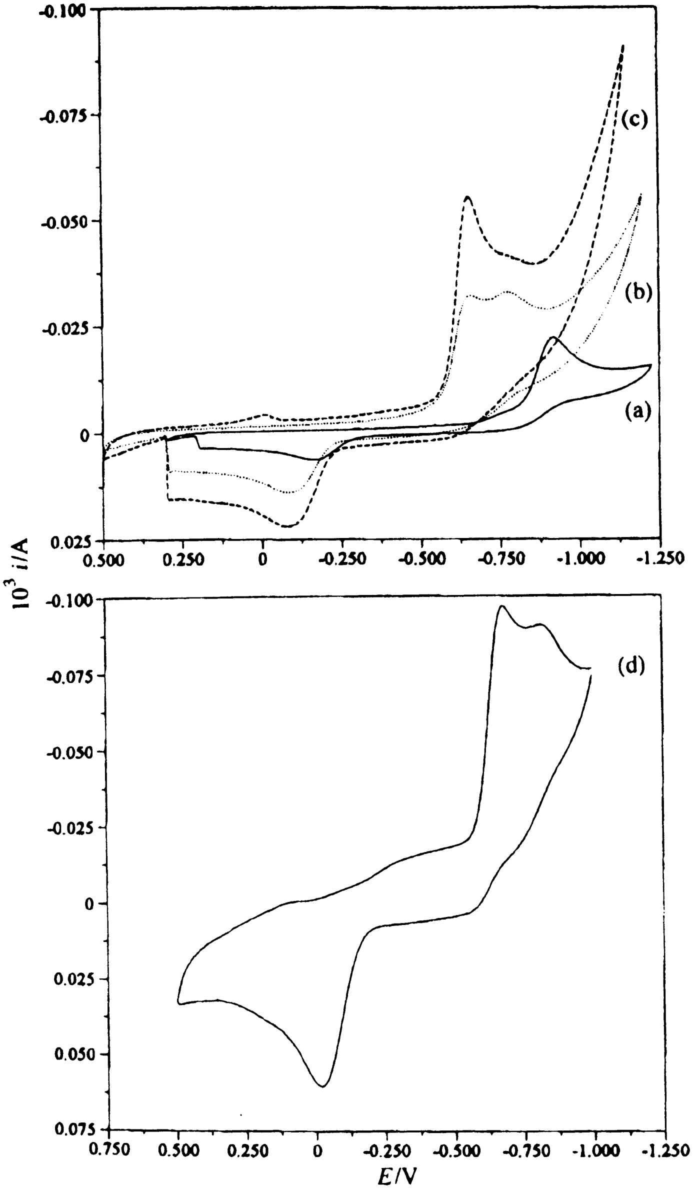
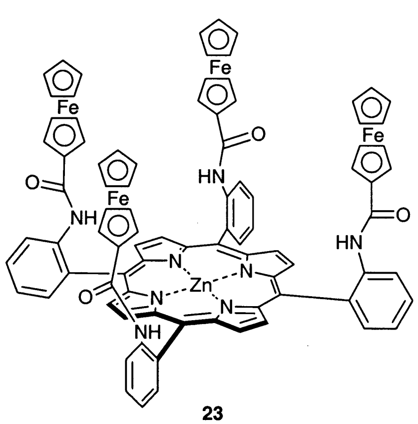


Fig. 9. CV of (a) **22**, (b) **22** in the presence of 0.6 equivalents NH_4BF_4 (c) **22** in the presence of 1.0 equivalent NH_4BF_4, and (d) **22** in the presence of 0.8 equivalents $NaBF_4$. (Reproduced with permission from J. Chem. Soc. Dalton Trans. (**1998**) 2289, Copyright 1998, The Royal Society of Chemistry.)



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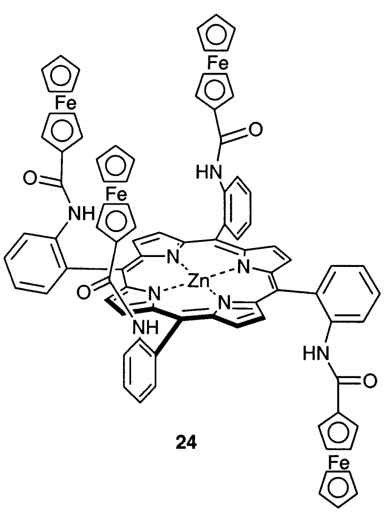

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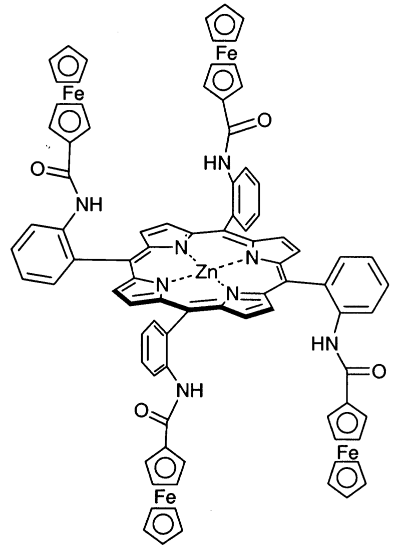

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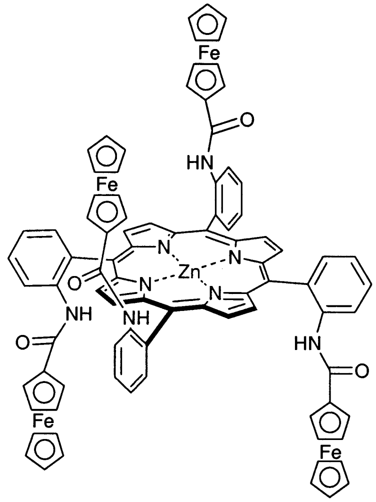

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Sessler and co-workers recently combined their anion binding calixpyrrole skeleton with a redox active ferrocene group [30]. Two new ferrocene-calixpyrrole conjugates were synthesized coupling ferrocenemethylamine with calixpyrrole *meso*- and β-carboxylic acids, producing compounds **27** and **28**, respectively. The receptors bound anions in dichloromethane-d_2 solution, however, the electrochemical properties of **27** and **28** became rather complicated in the presence of anions.

Table 5
Electrochemical data for compounds **27** and **28**

Anion[a]	Receptor **27**			Receptor **28**		
	K_a (M^{-1})[b]	$E_{1/2}$ (mV)[c]	ΔE (mV)	K_a (M^{-1})[b]	$E_{1/2}$ (mV)[c]	ΔE (mV)
No anion	n/a	511	n/a	n/a	503	n/a
$H_2PO_4^-$	40[d]	502	−9	40	534	31
F^-	[e]	525	14	1496	566	63
Cl^-	202	718	207	444	481	−22

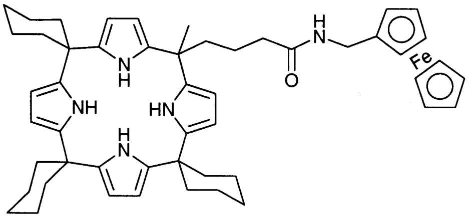
[a] Used in the form of their $(n\text{-}Bu_4N)^+$-salts.

[b] Association constants for anion binding; recorded in dichloromethane-d_2 errors <20%; determined from Δ(δ ppm) N*H*.

[c] Determined in dichloromethane containing 0.1 mol/l $(n\text{-}Bu_4NPF_6)$ as the supporting electrolyte. Solutions of **27**/**28** were 5×10^{-4} M and potentials were determined with reference to Ag | AgCl.

[d] This value was determined using the chemical shift of the β-CH of the pyrrole since the pyrrole–NH signal became too broad to be followed accurately during the titration.

[e] NMR signals became very broad in this case so that an accurate determination of this value was impossible.



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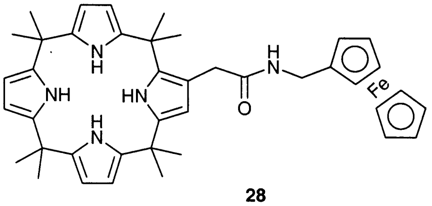

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Both anodic and cathodic shifts were observed upon the addition of anions to **27** and **28** (Table 5). No clear predictive conclusions could be reached as to the direction of a particular shift, although it was speculated that oxidation processes occurring at the calixpyrrole skeleton may be coupling to the ferrocene oxidation.

Beer and co-workers recently reported a series of neutral ferrocene amide and amine receptors **29**–**36** for sensing anionic species [31] The stability constants of compounds **29**–**33** were measured using ^{1}H-NMR titration techniques. The results are presented in Table 6. All of the receptor species showed evidence for anion binding while neutral. Receptor **32** showed a remarkable preference for binding HSO_4^- anions in chloroform-d with $K > 10\,000$ M^{-1}. This selectivity is due to two different modes of anion binding operating in the **32**–HSO_4^- complex. This anion is highly acidic and may protonate the amine group of the receptor. The guest is therefore bound by a combination of electrostatics and hydrogen bonds. $H_2PO_4^-$ is less acidic—and therefore will not protonate the amine group of the receptor, leading to a complex that is stabilized by hydrogen bonding alone, and is as a consequence, much weaker ($K = 120$ M^{-1}). The electrochemical properties of the receptors were studied by CV techniques. The $E_{1/2}$ values for **29**, **30**, **32**, **33**, **35** and **26** are shown in Table 7 and the shifts of the anodic wave in the presence of various

Table 6
Stability constants derived from proton NMR titrations (errors = 10%) measured at 25°C

Receptor	Solvent	Anion	K (M^{-1})
29	$CDCl_3$	Cl^-	4.7
29	$CDCl_3$	$H_2PO_4^-$	5.0[a]
30	$CDCl_3$	Cl^-	21
30	$CDCl_3$	$H_2PO_4^-$	6.0
31	$CDCl_3$	$H_2PO_4^-$	5.0[a]
31	$CDCl_3$	HSO_4^-	8.5[a]
32	$CDCl_3$	NO_3^-	15
32	$CDCl_3$	$H_2PO_4^-$	120
32	$CDCl_3$	HSO_4^-	> 10 000
32	CD_3CN	Cl^-	17
32	CD_3CN	$H_2PO_4^-$	130
32	CD_3CN	HSO_4^-	7500
33	$CDCl_3$	Cl^-	22.5
33	$CDCl_3$	Br^-	24
33	$CDCl_3$	I^-	23
33	$CD_3CN/CDCl_3$ (1:1)	Cl^-	29.5
33	DMSO	Cl^-	5.0

[a] Errors = 33% due to very weak titration profiles.

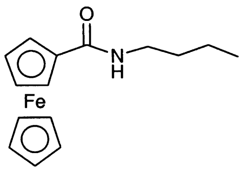
anions is shown in Table 8. In the presence of HSO_4^- the CV of compound **32** showed a new oxidation peak, cathodically shifted by 220 mV from that of the free receptor. In this case the binding event is communicated to the ferrocene moiety by a combination of through space and through bond interactions. Addition of chloride to the free receptor caused the oxidation peak to shift by only 35 mV. Other notable perturbations were seen with receptors **35** and **36**, both receptors showing large responses with $H_2PO_4^-$ anions (120 and 240 mV, respectively).

Table 7
Electrochemical data for free receptors measured at 25°C[a]

Receptor	Solvent	$E_{1/2}$ (V)
29	CH_3CN	0.18
30	CH_3CN	0.21
32	CH_3CN	0.27 0.70[b] (amine)
33	$CH_3CN/CHCl_3$ (1:1)	0.41
35	CH_3CN	0.22 0.95[b] (amine)
36	CH_3CN	0.49[b] 0.73[b] (amine)

[a] A glassy carbon working electrode was used together with a platinum gauze counter electrode. $E_{1/2}$ values quoted vs. the Ag | Ag^+ in MeCN reference electrode.

[b] irreversible redox wave; therefore E_{pa} quoted.



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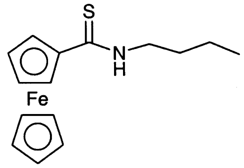

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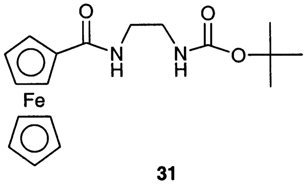

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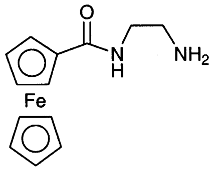

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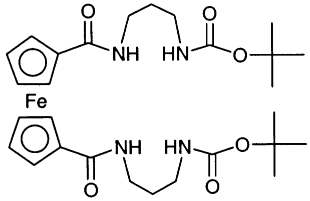

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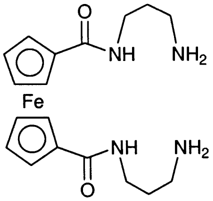

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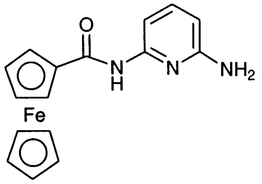

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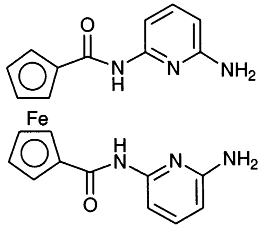
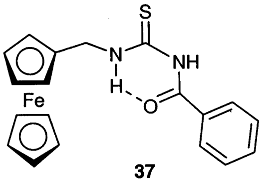


36

Ferrocene based anion receptors containing thiourea or guanidinium hydrogen bond donating receptors have also been produced [32]. Compound **37** was found not to interact with anions (due to an intramolecular NH···OC hydrogen bond forcing the molecule into an unfavourable conformation). This bond can not form in **38** and **39** and it was found that both these compounds bind anions. Cathodic shifts of up to 125 mV in the ferrocenium/ferrocene redox couple of **39** with

$H_2PO_4^-$ anions were observed in DMSO, presumably mediated via through space interactions. Compound **39** is capable of recognizing $P_2O_7^{4-}$ anions in methanol/water (a highly competitive solvent mixture) giving a cathodic shift of 70 mVin the ferrocene redox-wave.



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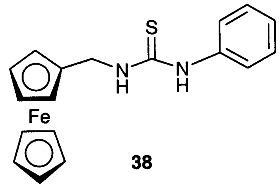

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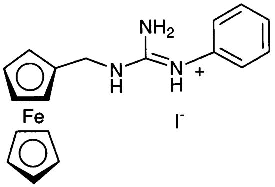

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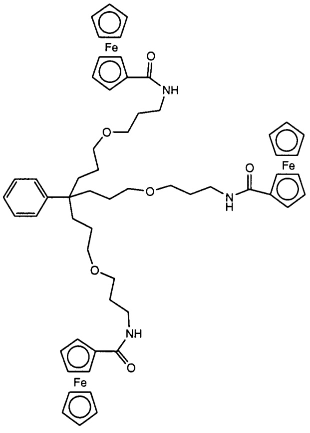
Astruc and co-workers have produced dendrimers containing three **40**, nine **41** and 18 **42** ferrocene units and found evidence for a dendritic effect in the recognition process (increasing ΔE values for increasing dendrimer size) [33]. The electrochemical data for these compounds are shown in Table 9. The largest perturbation for each dendrimer is observed on addition of $H_2PO_4^-$ anions, however, as the size of the dendrimer increases so does the perturbation caused by a particular anion. This is rationalized in terms of a dendrimer effect due to the dendrimer size and surface hole size through which the anion must pass.



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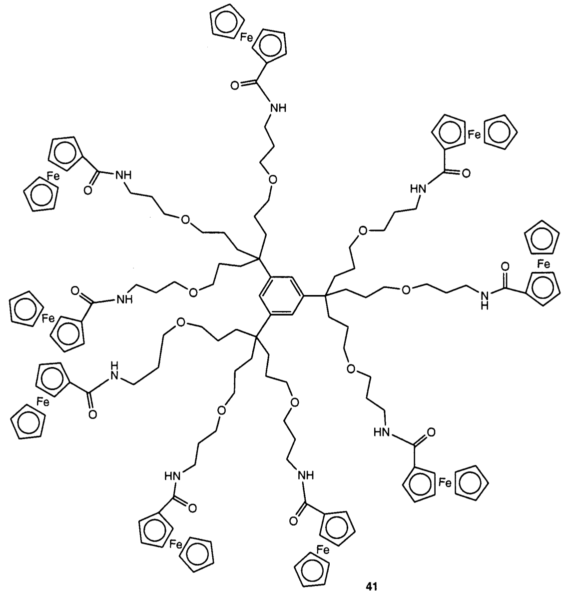

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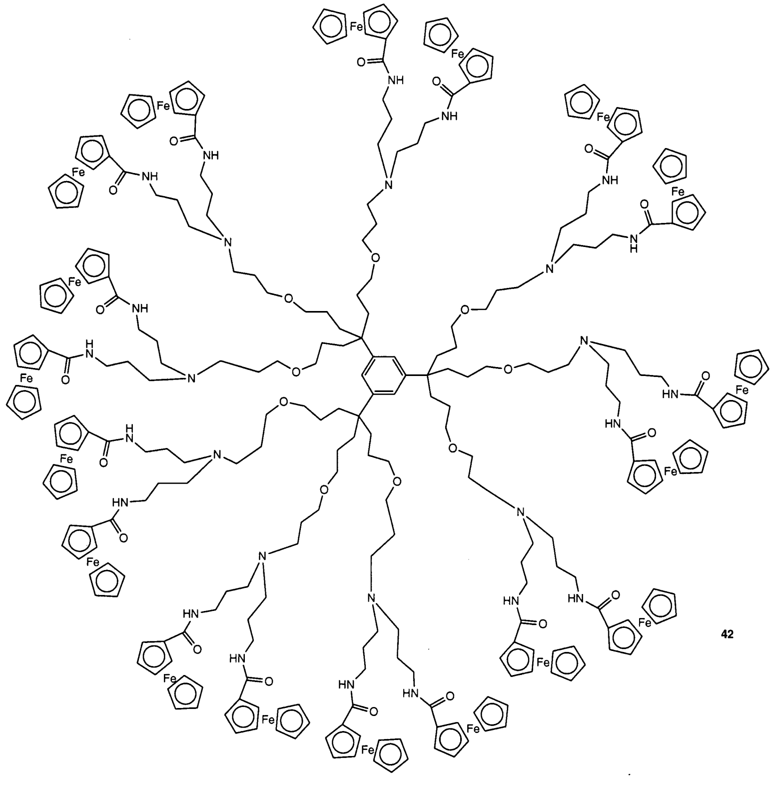

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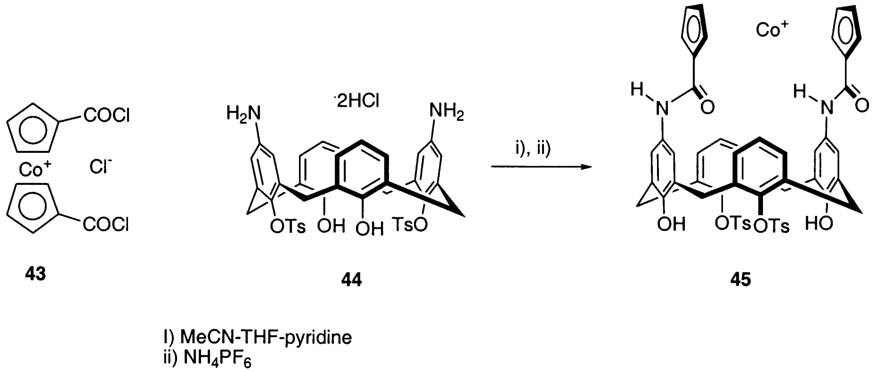
Table 8
Electrochemical response of receptors to anionic guests measured at 25°C

Receptor	Solvent	Anion	ΔE_{pa} [a] (mV)
29	CH_3CN	Cl^-	0
30	CH_3CN	Cl^-	0
32	CH_3CN	Cl^-	35
32	CH_3CN	$H_2PO_4{}^-$	165
32	CH_3CN	$HSO_4{}^-$	220
32	CH_3CN	$BrCH_2COOH$	0
33	$CH_3CN/CHCl_3$ (1:1)	Cl^-	80
33	$CH_3CN/CHCl_3$ (1:1)	Br^-	45
35	CH_3CN	Cl^-	10
35	CH_3CN	$H_2PO_4{}^-$	120
35	CH_3CN	$HSO_4{}^-$	5
36	CH_3CN	Cl^-	50
36	CH_3CN	$H_2PO_4{}^-$	240
36	CH_3CN	$HSO_4{}^-$	85

[a] Cathodic shift of oxidation peak after the addition of five equivalents of guest. A glassy carbon working electrode was used together with a platinum gauze counter electrode and a Ag | Ag^+ in MeCN reference electrode.

Table 9
Titration of the ferrocene dendrimers **40**–**42** by various n-Bu_4N^+ salts monitored by the variation ΔE (mV for one equivalent of anion per branch) of the standard redox potential of the redox couple in CV in dichloromethane vs. SCE

	40 (3-Fc) (mV)	**41** (9-Fc) (mV)	**42** (18-Fc) (mV)
$H_2PO_4^-$	110	220	315
HSO_4^-	30	65	130
Cl^-	<20	20	45
NO_3^-	<20	<20	30



Scheme 4. Synthesis of compound **45**.

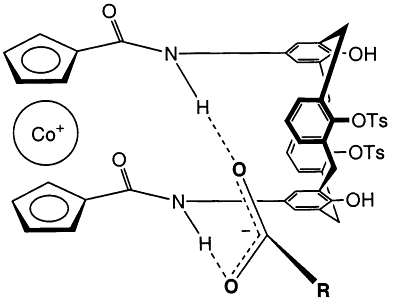


Fig. 10. The amide NH protons of **45** form a hydrogen bonding array that is complementary to carboxylate anions. The carboxylate is bound by a combination of these hydrogen bonds and an electrostatic interaction between the cobaltocenium cation and the carboxylate anion.

Beer and co-workers have produced a number of cobaltocenium based anion receptors since 1989. Recently a new cobaltocenium calixarene receptor **45** (Scheme 4) has been synthesized [34]. Condensation of 1,1′-bis(chlorocarbonyl)cobaltocenium chloride (**43**) with the calixarene upper rim bis-amine (**44**) afforded the upper rim bridged cobaltocenium calixarene **45** in 38% yield. This receptor contains both a positively charged cobaltocenium group and hydrogen bond donating amide functionalities that may both contribute to anion coordination. The amide NH groups form a bi-dentate hydrogen bonding array that is complementary to carboxylate anions (Fig. 10). The crystal structure of the chloride complex of the receptor shows the two amide bonds forming a binding site for the chloride anion (Fig. 11). The stability constants of **45** in DMSO-d_6 were investigated using ^{1}H-NMR titration techniques. As expected, carboxylate anions were bound to the receptor with large stability constants (Table 10). This high selectivity for carboxylates is reflected in the electrochemical properties of the receptor. On addition of carboxylate anions to acetonitrile solutions of **45**, substantial cathodic shifts of the reversible cobaltocenium–cobaltocene redox couple at 0.85V (vs. $Ag \mid Ag^+$) of up to 155 mV were observed (Table 11). Other anions produced much smaller shifts for example Cl^- caused a shift of 60 mV. An exception to this was $H_2PO_4^-$ that caused a shift of 130 mV. $H_2PO_4^-$ anions may also be bound in a bi-dentate fashion (this is reflected in the relatively high stability constant) and thus cause a larger perturbation in the cobaltocenium/cobaltocene redox couple. The mechanism of redox–binding coupling in this case is presumably a combination of through bond and through space interactions.

Anions receptors based on ruthenium–bipyridyl complexes have been shown to be both electrochemical and optical sensors for anions **46**–**51** [35]. All the receptors possess a macrocyclic core containing hydrogen bond donating NH groups. X-ray crystallographic investigations of a number of complexes show that this is where the anion is bound in the solid state. Cathodic shifts of the first substituted bipyridyl redox wave were monitored on addition of various anionic guests. Interestingly the other bipyridyl moieties are not significantly perturbed by the presence of anions—a finding that serves to confirm that the anion is bound within the macrocyclic core in solution. The bound anion is perturbing only the nearby substituted bipyridyl moiety and not the more distant unsubstituted ones.

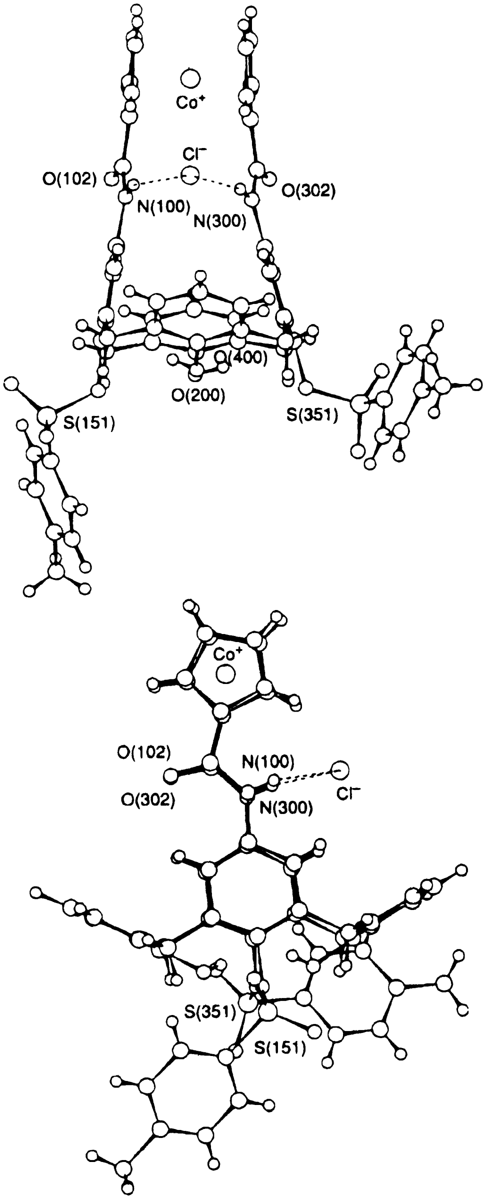


Fig. 11. The crystal structure of the chloride complex of **45**. (Reproduced with permission from Chem. Commun. (**1997**) 107, Copyright 1997, The Royal Society of Chemistry.)

Table 10
Stability constant data in DMSO-d_6 for compound **45**

Anion	K^a (M^{-1})
Cl^-	70
Br^-	[b]
NO_3^-	125
HSO_4^-	40
$H_2PO_4^-$	6380
$MeCO_2^-$	41 520
$PhCO_2^-$	38 400
$PhCH_2CO_2^-$	22 270
$C_{10}H_{17}CO_2^-$	19 750

[a] Errors estimated to be 10%.

[b] Very weak binding, a stability constant value could not be calculated in this solvent.

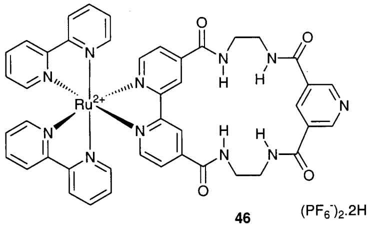
Cathodic shifts of up to 125 mV were observed for this redox process with compound **51** in acetonitrile solution on addition of Cl^- anions (a remarkable selectivity is shown for Cl^- anions over $H_2PO_4^-$ with **50** and **51**). A combination of through bond and through space interactions together with a possible direct coordination pathway mediated via bipy C–H···anion hydrogen bonds are responsible for communicating the binding event to the bipyridyl moiety.

Table 11
Electrochemical data[a] for compound **45**

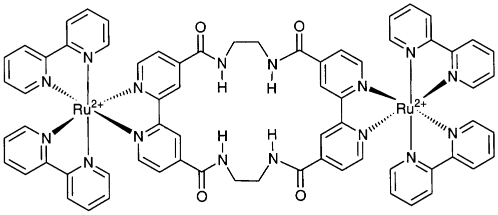
Anion	ΔE^b (mV)
Cl^-	60
NO_3^-	20
HSO_4^-	10
$H_2PO_4^-$	130
$MeCO_2^-$	155
$PhCO_2^-$	140
$PhCH_2CO_2^-$	150
$C_{10}H_{17}CO_2^-$	135

[a] Obtained in acetonitrile solution containing 0.1 mol dm^{-3} NBu_4PF_6 as the supporting electrolyte.

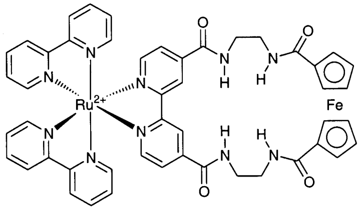
[b] Cathodic shift perturbations of cobaltocenium/cobaltocene redox couple produced by presence of anions (up to five equivalents) added as their n-Bu_4N salts.



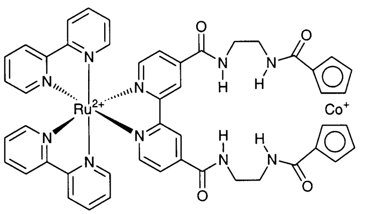
46 $(PF_6^-)_2 \cdot 2H_2O$



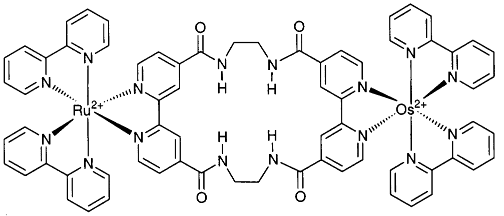
$(PF_6^-)_4 \cdot 4H_2O$ **50**



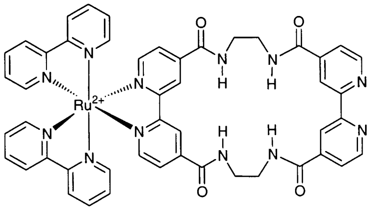
47 $(PF_6^-)_2 \cdot 2H_2O$



$(PF_6^-)_3 \cdot 3H_2O$ **48**

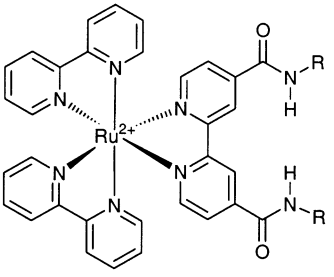


51 $(PF_6^-)_4 \cdot 4H_2O$



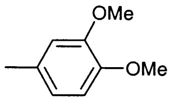
$(PF_6^-)_2 \cdot 2H_2O$ **49**

Other ruthenium–bipyridyl complexes with acyclic, macrocyclic and calixarene substituents have been synthesized and shown to coordinate to anions via hydrogen bonds [36]. The electrochemical properties of **52**–**56** are shown in Table 12. The calixarene receptor **56** selectively electrochemically senses $H_2PO_4^-$ (via through space and through bond mechanisms) in the presence of ten-fold excess amounts of HSO_4^- and Cl^-.

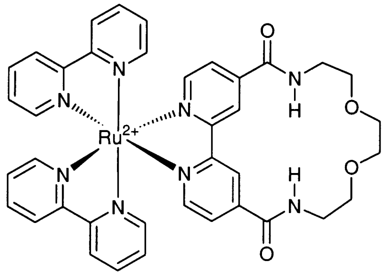


$(PF_6^-)_2.2H_2O$

52 R =

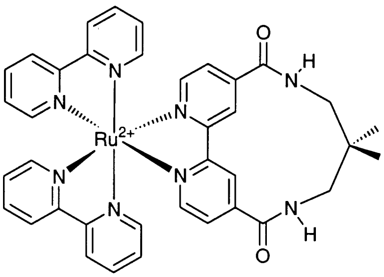


53 R = —$(CH_2)_2OMe$



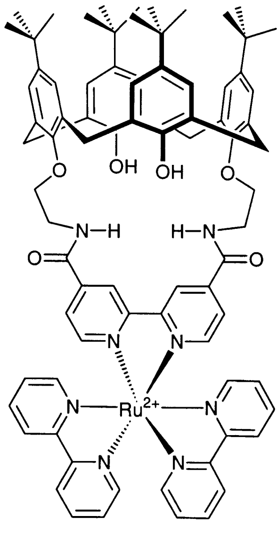
$(PF_6^-)_2.2H_2O$

54



55

$(PF_6^-)_2.2H_2O$



$(PF_6^-)_2.2H_2O$

56

Table 12
Electrochemical data for compounds **52**–**56**[a]

Receptor	Redox couples			
	Metal based RuII/III	bipy reductions		
		+2/+1	+1/0	0/−1
52	1.10	−1.40	−1.78	−2.02
53	1.12	−1.44	−1.80	−2.01
54	1.01	−1.48	−1.84	−2.06
55	1.02	−1.56	−1.87	−2.07
56	1.12	−1.40	−1.80	−2.01
	ΔE ($H_2PO_4^-$)[b] (mV)	ΔE (HSO_4^-)[b] (mV)	ΔE (Cl^-)[b] (mV)	ΔE (Br^-)[b] (mV)
52	[c]	[c]	40	30
53	130	15	65	60
54	175		70	10
55	150	20	65	
56	175	15	70	60

[a] Obtained in acetonitrile solution containing 0.1 mol dm^{-3} n-Bu_4NPF_6 as the supporting electrolyte. Solutions were ca. 5×10^{-4} mol dm^{-3} in receptor, and potentials were determined with reference to a $Ag^+ | Ag$ electrode (330 ± 5 mV vs. SCE) at 21 ± 1°C at 50 mV s^{-1} scan rate.

[b] Cathodic shift perturbations of the first ligand centred reduction couple produced by the presence of anions (up to ten equivalents) added as their tetrabutylammonium salts.

[c] Precipitation of complex prevented a ΔE value from being obtained.

6. Electrochemical recognition of neutral species

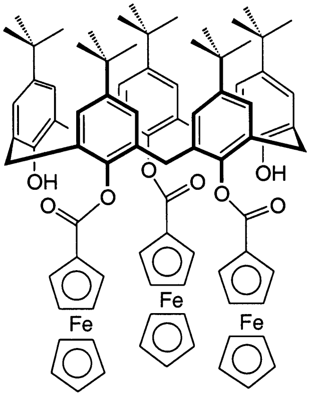
Perhaps surprisingly, the electrochemical detection of neutral guests by redox-active receptor species has attracted less attention than the detection of cations or anions and there are still few examples in the literature.

Beer and co-workers have used a 1-, 3-, 4-trisferrocene substituted calix[4]arene as a neutral guests sensor [37]. Electrochemical studies of the behaviour of **57** have been carried out using cyclic and square wave voltammetric techniques. The receptor itself undergoes two quasi-reversible oxidations at $E_{p1} = +350$ mV and $E_{p2} = +450$ mV referenced to $Ag | Ag^+$. Rotating disk electrode electrochemistry was used to resolve the two oxidation processes and it was found that one ferrocene was oxidised at 350 mV while the other two were oxidized at the larger anodic potential of 450 mV.

Preliminary electrochemical investigations on the effects of addition of potential neutral guests (DMF, DMSO, ethanol) to an electrochemical solution of **57** in CH_2Cl_2 show an interesting electrochemical effect. Addition of polar solvents such as DMF cause the two redox couples to merge. Similar effects were also observed on addition of DMSO or ethanol. However on addition of toluene to the electrochemical solution no shifts in the redox couples were observed.

The dielectric constant of CH_2Cl_2 is 8.9. Addition of DMF ($e = 36.7$) causes the peaks to merge however the addition of toluene ($e = 2.4$) causes little change in the CV. It may therefore be deduced that the splitting of the peak in CH_2Cl_2 alone is at least partially due to the interaction between the ferrocene moieties. The decrease in the interaction upon addition of the higher dielectric constant solvent implies that the polar solvent is interposing itself between the ferrocene moieties. As the dielectric constant of the interposed solvent increases, the shielding between the ferrocene centres increases due to the guest's higher polarisability.

The inclusion of the more highly polarisable guest therefore interferes with the electrochemical interactions present in the host so producing an electrochemical response.



57

Recently Tucker and co-workers synthesised the mono- and bis-pyridine amidoferrocene compounds **58** and **59** [38]. These receptors contain hydrogen bonding arrays that are complementary to carboxylic acids. ^{1}H-NMR titration studies of **58**

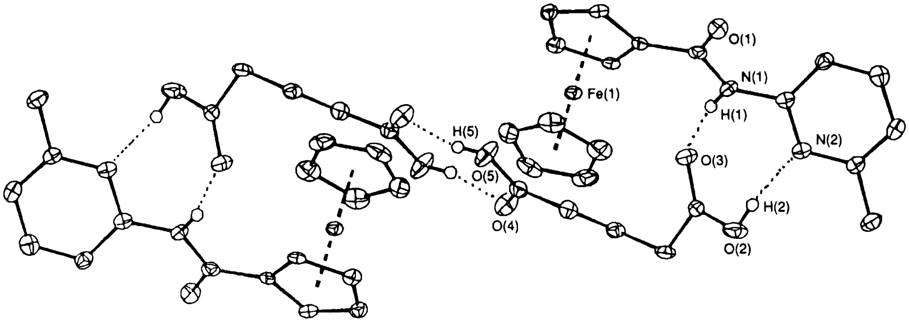
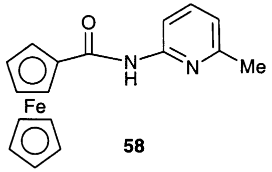
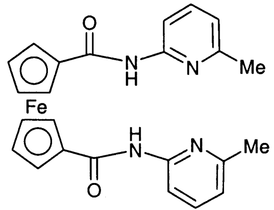


Fig. 12. Crystal structure of [**58**–**61**]$_2$ (the dotted lines indicate strong hydrogen bonds between the two species and also between a pair of acid molecules). (Reproduced with permission from Chem. Commun. (**1997**) 1649, Copyright 1997, The Royal Society of Chemistry.)

and **59** in chloroform-d with mono-carboxylic acids **60a–c** and glutaric acid **61** gave evidence for complexation in solution. Analysis of the titration data of **58** and **59** with monocarboxylic acids **60a–c** showed that 1:1 and 1:2 receptor–acid complexes were formed as expected. Titration of **58** with glutaric acid **61** initially gives a 2:1 receptor–acid complex and then a 1:1 complex on addition of an excess of the acid. The complex formed between **59** and **61** is proposed to be a four point hydrogen bonding interaction where one di-acid molecule is bound to one molecule of compound **59**, bridging the pyridine rings. The stability constant of this complex was found to be 10^4 M^{-1}.



58



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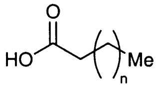
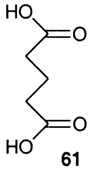


60a n = 1
60b n = 4
60c n = 7



61

The crystal structure of the complex $(\mathbf{58}\text{–}\mathbf{61})_2$ is shown in Fig. 12. Amide N–H hydrogen bond donation and pyridine N hydrogen bond acceptance allow the carboxylic acid group to be bound in a bi-dentate fashion. The crystal structure shows that in the solid state a carboxylic acid dimer is formed in the complex.

The electrochemical properties of **58** and **59** are shown in Table 13. Protonation of the receptors on addition of the carboxylic acids was discounted as addition of H^+ lead to large positive shifts in the redox waves of **58** and **59**. The shifts observed are consistent with the ferrocenium cation increasing the acidity of the amide N–H bond (and hence more strongly binding the carboxylic acid). The largest shift was observed on addition of glutaric acid to compound **59**. This is attributed to the formation of the four strong hydrogen bonding interactions, together with the enforcement of a particular geometry in the complex by the di-acid guest.

7. Conclusions

This short review has covered recent advances in the electrochemical recognition of cations, anions and neutral guest species by redox-active receptor molecules. The mechanisms of complexation–redox coupling via through bond, through space, and

Table 13
Electrochemical data for compounds **58** and **59** in dichloromethane in the absence and presence of neutral guest substrates **60a**–**c** and **61**[a]

Compound[b]	$E_{1/2}$ (V)	ΔE (mV)[c]			
		60a	**60b**	**60c**	**61**
58	+0.24	−20	−20	−25	−20
59	+0.44	−60	−55	−55	−85

[a] CVs were carried out at a scan rate of 200 mV s^{-1} in dichloromethane containing tetrabutylammonium perchlorate as the supporting electrolyte (0.1 M), ferrocene as internal reference (ca. 1 mM) and the appropriate ferrocene receptor (1 mM) at room temperature. The following electrode system was used: Pt wire working electrode, Pt wire counter electrode and Ag wire pseudo reference electrode.

[b] Redox potentials were referenced to ferrocene as an internal standard. For each voltammogram, the reversibility of the redox wave matched that of the ferrocene internal reference.

[c] The cathodic shift (mV) of the reversible couple of **58** or **59** upon addition of excess substrate.

direct coordination have been highlighted in each case. Over recent years there have been few papers reporting examples of receptors employing the conformational change mechanism [11]. The interference mechanism also remains to be exploited [37]. This is clearly an area of electrochemical molecular recognition that is full of opportunity for the interested chemist. We hope to see the emergence, over the next few years, of 'real-world' devices based on the concepts illustrated here.

References

[1] P.L. Boulas, M. Gomez-Kaifer, L. Echegoyen, Angew. Chem. Int. Ed. Engl. 37 (1998) 216.
[2] P.D. Beer, Adv. Inorg. Chem. 39 (1992) 79.
[3] A.E. Kaifer, S. Mendoza, in: G.W. Gokel (Ed.), Comprehensive Supramolecular Chemistry, vol. 1, Elsevier, Oxford, 1996, p. 701.
[4] P.D. Beer, Chem. Soc. Rev. 18 (1989) 409.
[5] A.E. Kaifer, L. Echegoyen, in: Y. Inoue and G.W. Gokel (Eds.), Redox Control of Cation Binding in Macrocyclic Systems, Marcel Dekker, New York, 1990.
[6] T.E. Edmonds, in: T.E. Edmonds (Ed), Chemical Sensors, Blackie, Glasgow, 1988, p. 193.
[7] P.D. Beer, P.A. Gale, Z. Chen, Adv. Phys. Org. Chem. 31 (1998) 1.
[8] T. Saji, Chem. Lett. (1986) 275.
[9] P.D. Beer, C. Blackburn, J.F. McAleer, H. Sikanyika, Inorg. Chem. 29 (1990) 378.
[10] P.D. Beer, P.A. Gale, Z. Chen, M.G.B. Drew, J.A. Heath, M.I. Ogden, H.R. Powell, Inorg. Chem. 36 (1997) 5880.
[11] P.D. Beer, Z. Chen, A. Grieve, J. Haggitt, J. Chem. Soc. Chem. Commun. (1994) 2413.
[12] P.D. Beer, Z. Chen, M.G.B. Drew, P.A. Gale, J. Chem. Soc. Chem. Commun. (1995) 1851.
[13] J. Osteryoung, J.J. O'Dea, in: A.J. Bard (Ed.), Electroanalytical Chemistry, New York: Marcel Dekker, 1987.
[14] M.C. Grossel, D.G. Hamilton, J.I. Fuller, E. Millan-Barios, J. Chem. Soc. Dalton. Trans. (1997) 3471.
[15] H. Plenio, D. Burth, Organometallics 15 (1996) 4054.
[16] H. Plenio, D. Burth, Organometallics 15 (1996) 1151.
[17] H. Plenio, C. Aberle, Organometallics 16 (1997) 5950.

[18] H. Plenio, C. Aberle, Angew. Chem. Int. Ed. Engl. 37 (1998) 1397.

[19] A. Chesney, M.R. Bryce, A.S. Batsanov, J.A.K. Howard, L.M. Goldenberg, Chem. Commun. (1998) 677.

[20] P.D. Beer, Z. Chen, M.G.B. Drew, J.E. Kingston, M.I. Ogden, P. Spencer, J. Chem. Soc. Chem. Commun. (1993) 1046.

[21] P.D. Beer, Z. Chen, M.G.B. Drew, A.O.M. Johnson, D.K. Smith, P. Spencer, Inorg. Chim. Acta 246 (1996) 143.

[22] M.J.L. Tendero, A. Benito, R. Martínez-Máñez, J. Soto, J. Payà, A.J. Edwards, P.R. Raithby, J. Chem. Soc. Dalton Trans. (1996) 343.

[23] A. Benito, R. Martínez-Máñez, J. Soto, M.J.L. Tendero, J. Chem. Soc. Faraday Trans. (1997) 2175.

[24] M.E. Padilla-Tosta, R. Martínez-Máñez, T. Pardo, J. Soto, M.J.L. Tendero, Chem. Commun. (1997) 887.

[25] J.M. Lloris, R. Martínez-Máñez, T. Pardo, J. Soto, A.E.P. Padilla-Tosta, Chem. Commun. (1998) 837.

[26] P.D. Beer, D.K. Smith, J. Chem. Soc. Dalton Trans. (1998) 417.

[27] Z. Chen, A.J. Pilgrim, P.D. Beer, J. Electroanal. Chem 444 (1997) 209.

[28] D.S. Shephard, B.F.G. Johnson, J. Matters, S. Parsons, J. Chem. Soc. Dalton Trans. (1998) 2289.

[29] P.D. Beer, Chem. Commun. (1996) 689.

[30] J.L. Sessler, A. Gebauer, P.A. Gale, Gazz. Chim. Ital. 127 (1997) 723.

[31] P.D. Beer, A.R. Graydon, A.O.M. Johnson, D.K. Smith, Inorg. Chem. 36 (1997) 2112.

[32] P.D. Beer, M.G.B. Drew, D.K. Smith, J. Organomet. Chem. 543 (1997) 259.

[33] C. Valéro, J.-L. Fillaut, J. Ruiz, J. Guittard, J.-C. Blais, D. Astruc, J. Am. Chem. Soc. 119 (1997) 2588.

[34] P.D. Beer, M.G.B. Drew, D. Hesek, K.C. Nam, Chem. Commun. (1997) 107.

[35] P.D. Beer, F. Szemes, V. Balzani, C.M. Salà, M.G.B. Drew, S.W. Dent, M. Maestri, J. Am. Chem. Soc. 119 (1997) 11864.

[36] F. Szemes, D. Hesek, Z. Chen, S.W. Dent, M.G.B. Drew, A.J. Goulden, A.R. Graydon, A. Grieve, R.J. Mortimer, T. Wear, J.S. Weightman, P.D. Beer, Inorg. Chem. 35 (1996) 5868.

[37] P.D. Beer, P.A. Gale, Z. Chen, M.G.B. Drew, Supramol. Chem 7 (1996) 241.

[38] J.D. Carr, L. Lambert, D.E. Hibbs, M.B. Hursthouse, K.M.A. Malik, J.H.R. Tucker, Chem. Commun. (1998) 1649.