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Transition metal and organometallic anion complexation agents

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Contents

Abstract . . . 167
1. Introduction . . . 167
2. Electrochemical recognition of anions . . . 168
  2.1 Cobaltocenium-based anion receptors . . . 168
  2.2 Ferrocene-based anion receptors . . . 170
  2.3 Arene and other organometallic receptors . . . 178
3. Optical sensors for anions . . . 178
  3.1 Ruthenium(II)- and rhenium(I)-bipyridyl-based receptors . . . 178
  3.2 Other optical sensors . . . 182
4. Recent new directions in anion sensing . . . 186
5. Conclusions . . . 187
Acknowledgements . . . 188
References . . . 188

Abstract

Anions are ubiquitous species, and therefore, their sensing is of considerable interest. Anion receptors containing electrochemically active groups such as ferrocene or cobaltocenium, or optically active groups such as ruthenium(II) bipyridyl derivatives, allow the binding of anions to be detected by a physical response at the metal centre. These systems have been incorporated into various acyclic, macrocyclic and calix[4]arene frameworks, many of which include an amide hydrogen-bonding group. Anions may be recognised in a range of environmental conditions, with some receptors even being active in aqueous solution. The incorporation of new transition metal and organometallic systems has led to the development of several new strategies in anion recognition.

Keywords: Anion recognition; Electrochemical sensors; Optical sensors

1. Introduction

Anions play numerous indispensable roles in biological and chemical processes, as well as contributing significantly to environmental pollution. For instance, the majority of enzyme substrates and co-factors are anionic [1], as is DNA itself. Excess amounts of anionic pollutants such as phosphate and nitrate lead to eutrophication and consequent disruption of aquatic life cycles [2]. Radioactive pertechnetate from the nuclear fuel cycle may also contribute to pollution [3].

Given their importance, there has obviously been much effort expended in the design of anion complexing reagents. The main strategies have focused on cationic polyammonium, guanidinium, quaternary ammonium, expanded porphyrin host systems, and a variety of Lewis acidic containing receptors such as tin, boron, silicon, mercury and uranyl. Neutral organic receptors that bind anions solely via favourable hydrogen bonding

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interactions have also been recently exploited. Reviews on various aspects of anion coordination can be found in the references [4–8], and also elsewhere in this volume. This review deals with recent developments in the design of anion receptors containing transition metal and organometallic components. Such receptors are designed so that they can selectively bind and sense the anion recognition event via a macroscopic physical response from the inorganic redox or photo-active moiety.

Significant progress has been made in the synthesis of similar receptors for cationic species. However, the nature of anions makes receptor design more challenging. Anions are larger than isoelectronic cations, and therefore have a lower charge to radius ratio. This decreases the effectiveness of electrostatic binding. Anionic species display a wide range of geometries, and therefore, a higher degree of receptor design may be required for host:guest complementarity. Also, anions are sensitive to pH conditions, and so receptors must function within the pH window of the target anion. Solvent effects are a crucial consideration, since anions are often highly solvated. Potential receptors are in effect competing with the solvent environment in which the anion recognition event takes place [6,9].

This review article will provide an overview of receptor systems that incorporate a transition metal or organometallic subunit, and exhibit a physical response to anion recognition, and also detail current developments in this field.

2. Electrochemical recognition of anions

2.1. Cobaltocenium-based anion receptors

The cobaltocenium moiety has been studied extensively in the context of redox-responsive anion receptors. The first class of anion receptor based on this system was reported by Beer and coworkers in 1989 [10]. The ester functionalized bis-cobaltocenium macrocyclic receptor **1** bound and electrochemically sensed bromide in acetonitrile via favourable electrostatic interactions.

Amide functionalities were appended to the cobaltocenium moiety to provide hydrogen bond donors capable of coordinating anions, such as in receptors **2** and **3** in Fig. 1 [11]. Proton NMR anion titration studies in d_6-DMSO reveal considerable downfield shifts, particularly for the amide protons, indicative of a strong hydrogen-bonding interaction. Both receptors **2** and **3** selectively bind dihydrogenphosphate over chloride in CD_3CN, with differences in stability constant of approximately an order of magnitude ($K(H_2PO_4^-)$ 1200 M^{-1} and $K(Cl^-)$ 100 M^{-1} for **2**, $K(H_2PO_4^-)$ 320 M^{-1} and $K(Cl^-)$ 35 M^{-1} for **3**) [12]. This selectivity may be attributed to the greater basicity of the $H_2PO_4^-$ anion.

These receptors are also capable of electrochemically recognising anions. Addition of an anionic guest stabilises the positive cobalt centre, resulting in substantial cathodic shifts of the reversible Cp_2Co^+–Cp_2Co redox couple. Dihydrogenphosphate induces cathodic shifts of 200 and 240 mV, respectively, for receptors **2** and **3**, whereas chloride produces shifts of lower magnitude, 30 and 85 mV, respectively. This complements the higher binding constants obtained via NMR for the $H_2PO_4^-$ anion.

The importance of the amide hydrogen-bonding interaction has been highlighted by studies with cobaltocenium receptors containing tertiary amides [13]. These receptors exhibit negligible anion binding. Crystal structure analysis of the bromide complex of receptor **2** clearly shows hydrogen bonds to the amide proton, as well as to Cp and aryl protons.

Receptors **4** and **5** have been used to demonstrate an anionic macrocyclic effect. The macrocyclic receptor **4** shows a complex stability constant with chloride of $K = 250$ M^{-1} in DMSO, whereas the acyclic **5** has only $K = 20$ M^{-1} [14].

Ditopic bis-cobaltocenium receptors were synthesised in an attempt to enhance both selectivity and complex stability [12]. The two metallocenes are separated by various alkyl and aryl spacers, as shown in Fig. 2. ^{1}H-NMR titrations revealed that the receptors with alkyl spacers **6**–**8** all bound halide anions in CD_3CN in a 1:1 complex, with a preference for chloride. However, increasing the length of the alkyl chain leads to an overall decrease in stability constant, and also in the degree of selectivity (Table 1). Receptor **9** formed 2:1 complexes with anions, presumably due to the increased size of the cleft cavity. Electrochemical measurements for all receptors showed considerable cathodic shifts in the cobaltocenium redox wave with a variety of anions. Dihydrogenphosphate produced the largest shift, a cathodic perturbation of 165 mV.

A novel cobaltocenium porphyrin receptor **10** has been synthesised [15], in which four metallocenes are appended to the porphyrin. Fig. 3 shows the *cis*-α,α,α,α-atropisomer, which exhibits the selectivity trend $Cl^- > Br^- \gg NO_3^-$. Proton NMR titrations in acetonitrile showed shifts of up to 0.7 ppm for the amide, Cp and pyrrole protons upon addition of halide anions. Chloride and bromide bound in 1:1 stoichiometry, and gave stability constants of 860 and 820 M^{-1}, respectively, whereas nitrate exhibited weaker binding with $K = 190$ M^{-1}. The selectivity is atropisomer-dependent. The molecule exhibits complicated electrochemistry, with multiple redox waves due to both the cobaltocenium and the porphyrin. Addition of anions to acetonitrile solutions of **10** resulted in cathodic shifts of the cobaltocenium redox couple of 35–75 mV for chloride, bromide and hydrogensulphate, and 225 mV for dihy-

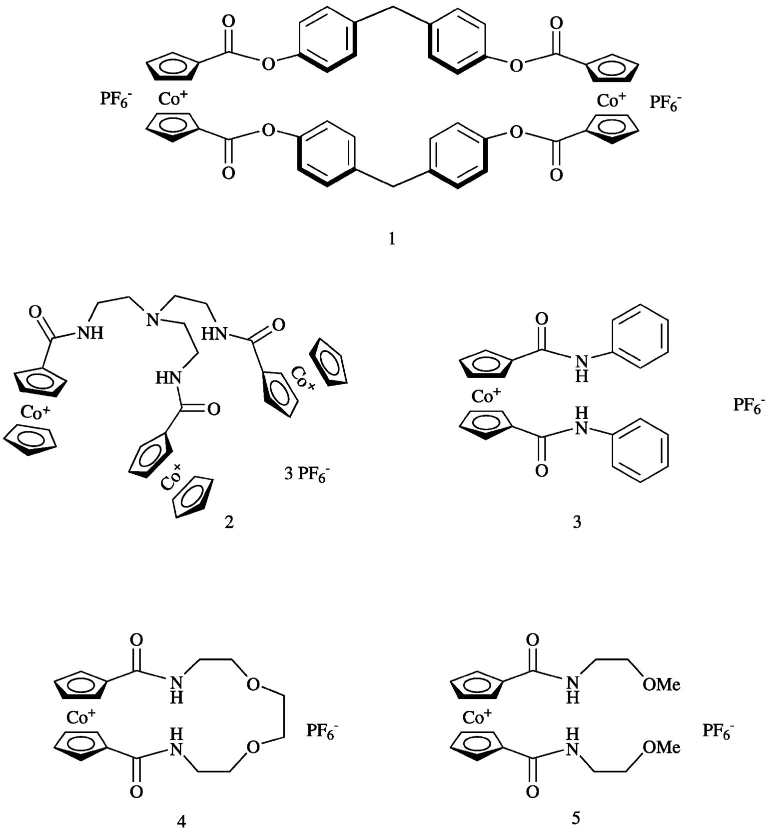

Fig. 1. Amide-functionalised cobaltocenium-based receptors.

drogenphosphate. Smaller shifts were observed for the porphyrin oxidation redox couple.

Crown ethers have also been appended to cobaltocenium, resulting in receptor **11** in which anion binding is switched on or off by potassium cations [16]. Proton NMR titrations with halides in acetonitrile gave log K values of 3.1 for chloride and 3.0 for bromide. Electrochemical titrations showed cathodic shifts of 60 and 30 mV for chloride and bromide. However, when both sets of NMR and electrochemical chloride anion titrations were repeated in the presence of K^+, no significant shifts were observed. It is proposed that addition of K^+ leads to the formation of a sandwich complex between the two crowns, which changes the conformation of the amide groups, and makes them less available for anion binding (Fig. 4).

Table 1
Stability constant data for **6**–**9** and halide anions in CD_3CN

Receptor	K (M^{-1}) [a]		
	Cl^-	Br^-	I^-
6	2500	330	450
7	1300	270	275
8	280	260	100
9	K_1 1260, K_2 250 [b]	K_1 1000, K_2 65 [b]	

[a] Errors estimated to be ≤10%.
[b] Errors estimated to be ≤15%.

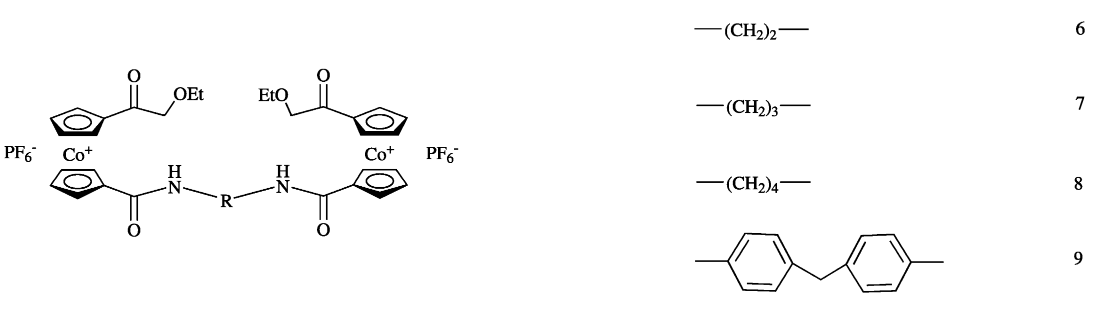

Fig. 2. Ditopic bis-cobaltocenium receptors.

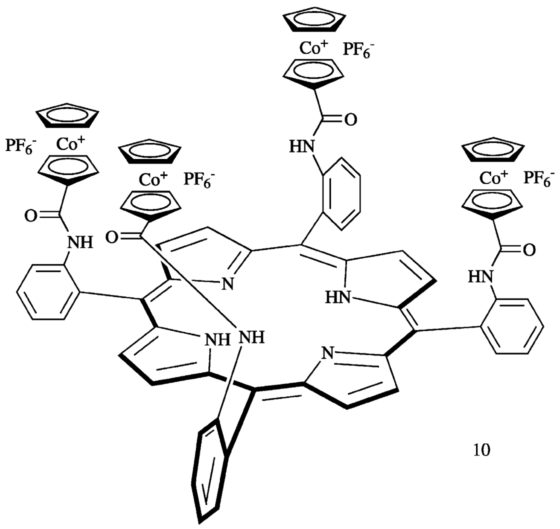

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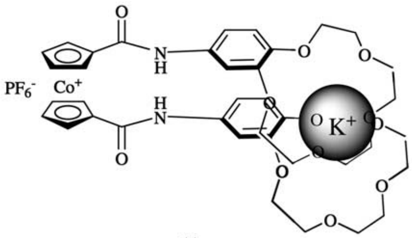
Fig. 3. Cobaltocenium porphyrin receptor.



11

Fig. 4. Cobaltocenium crown-ether receptors.

A variety of novel calix[4]arene receptors **12**–**14** (Fig. 5) have been prepared [17–19], and it has been shown that the anion-coordination properties are dependent upon the degree of upper rim preorganisation. For instance, **12** binds acetate much better than dihydrogenphosphate in DMSO, whereas the trend is reversed with the isomeric **13**. The bridged cobaltocenium calix[4]arene (**14**) forms thermodynamically more stable complexes with carboxylate and $H_2PO_4^-$ than either **12** or **13**. The receptor has notable selectivity for acetate, with a cathodic perturbation of $\Delta E = 155$ mV (Fig. 6). The crystal structure of the chloride complex of **14**, shown in Fig. 7, shows that the upper rim bidentate amide group provides a hydrogen bond cavity suitable for complexing bidentate anions such as carboxylates.

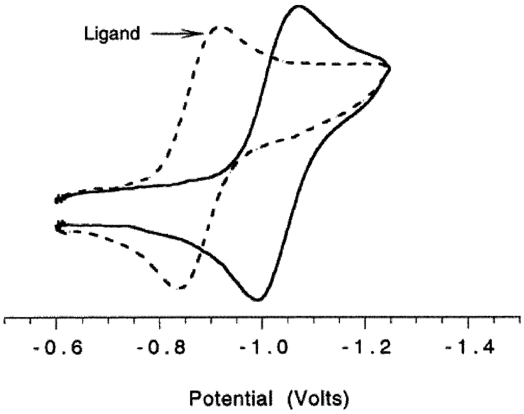
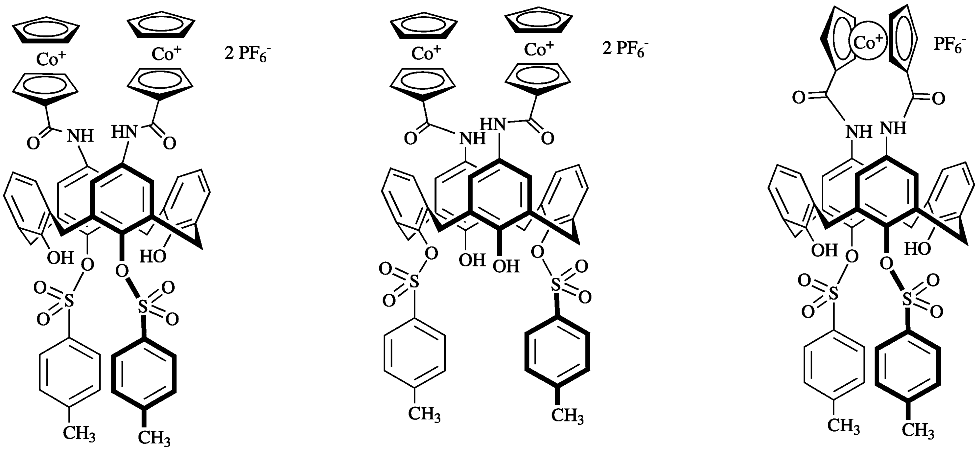


Fig. 6. Cyclic voltammograms of **14** in CH_3CN in the absence (---) and presence (-) of 3 equivalent of Bu_4NCO_2Me. Reproduced with permission from [19]. Copyright 1999, American Chemical Society.

2.2. *Ferrocene-based anion receptors*

The ferrocene moiety has also been used in the sensing of anions, with many of the receptors similar in design to the cobaltocenium molecules. One of the significant differences is that the ferrocene analogues are neutral, and therefore, have no inherent electrostatic interaction. NMR determined stability constants are, thus, lower in magnitude. The ferrocene does not directly interact with the anion until it is oxidised to ferrocenium, when electrostatic interactions are ‘switched on’ [20,21].

A range of receptors incorporating ferrocene units with secondary amides is shown in Fig. 8 [20,21]. Molecules **15**–**18** exhibited $H_2PO_4^-$-induced cathodic



12 13 14

Fig. 5. Cobaltocenium–calixarene receptors.

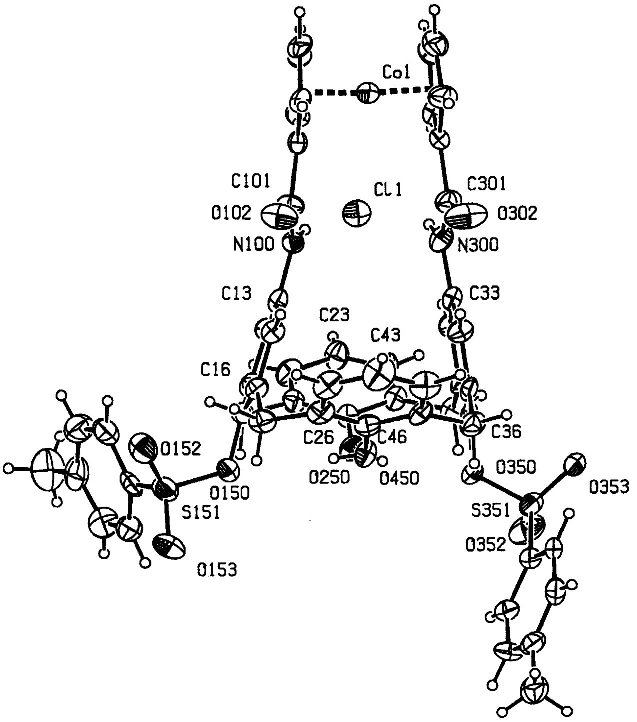
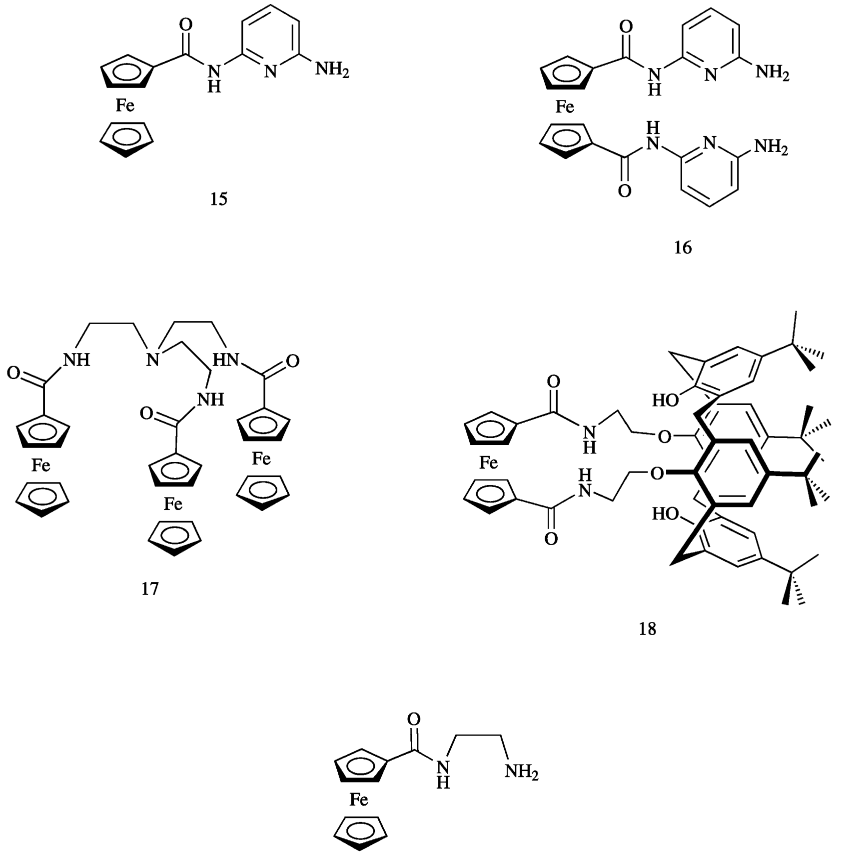


Fig. 7. The X-ray crystal structure of the chloride complex of receptor **14**. Reproduced with permission from [19]. Copyright 1999, American Chemical Society.

shifts of up to 240 mV in acetonitrile in the presence of a 10-fold excess of HSO_4^- and Cl^-. Receptor **19** on the other hand, exhibits selectivity for HSO_4^- in the presence of $H_2PO_4^-$, with a shift of 220 mV. The HSO_4^- anion protonates the basic amine functionality, which then binds the SO_4^{2-} anion.

In a similar approach, Moutet and coworkers have synthesised a range of amide-containing ferrocenyl ligands **20**–**24** in Fig. 9 [22]. Receptors **23** and **24** have several amide and ferrocene functionalities in close proximity, due to the cyclotriveratrylene structural unit. These receptors exhibit two-wave behaviour in the presence of $H_2PO_4^-$ and ATP^{2-} anions, with shifts of up to 260 mV in CH_3CN/CH_2Cl_2 mixtures. This group has also investigated the very simple receptor **25** [23], which is able to electrochemically sense dihydrogen phosphate and ATP anions in a range of solvents, including a negative shift of 470 mV in CH_2Cl_2 with $H_2PO_4^-$. This sensing ability is mainly a consequence of the strong ion-pairing interaction, and highlights the importance of such interactions in anion binding.

A ferrocene–zinc metalloporphyrin receptor **26** (Fig. 10) has been prepared, in which anions are bound via the Lewis acidic zinc centre and amide hydrogen bonding [24]. As with the cobaltocenium analogue, the atropisomer dictates the selectivity, and anion com-



15

16

17

18

19

Fig. 8. Ferrocene-amide based receptors.

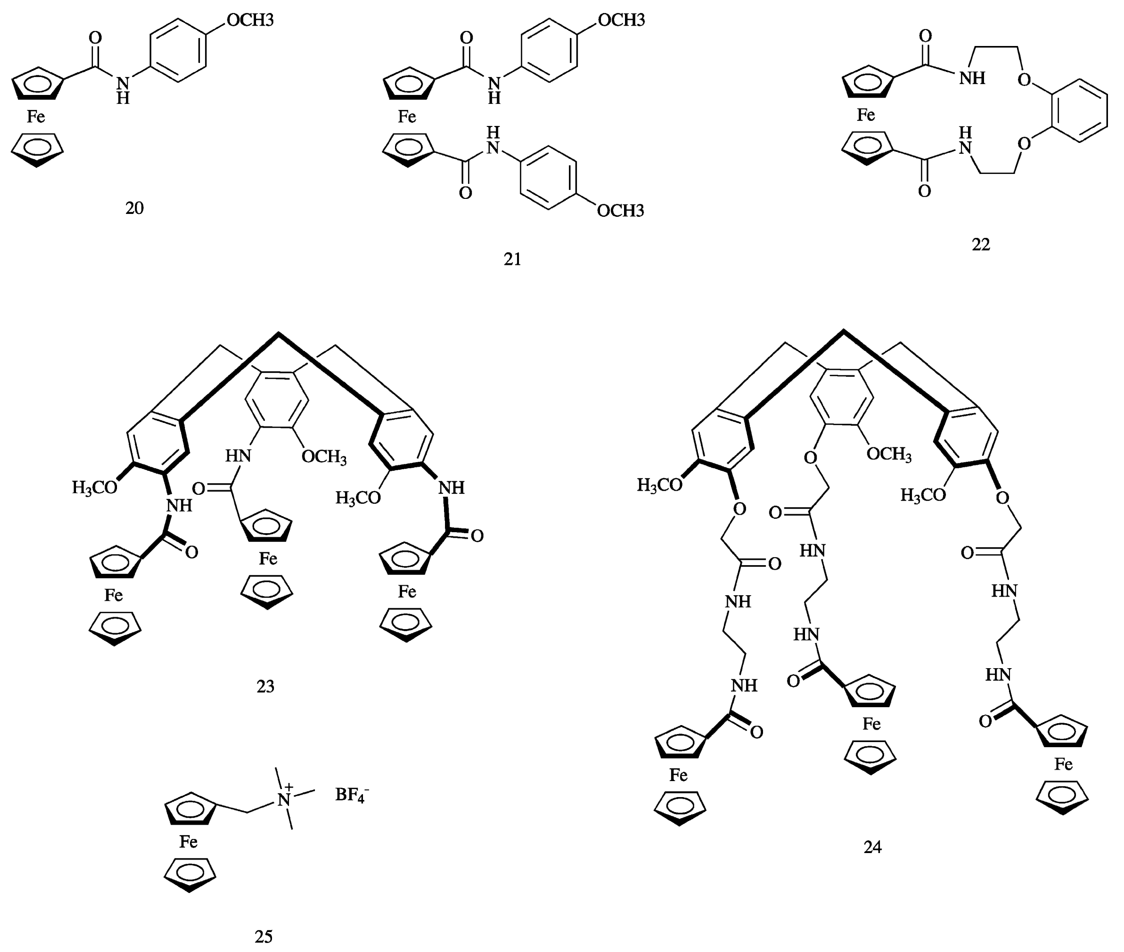


Fig. 9. More ferrocene-amide based receptors.

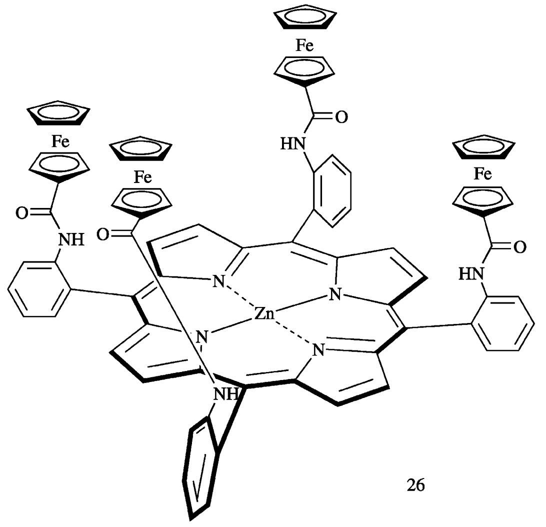
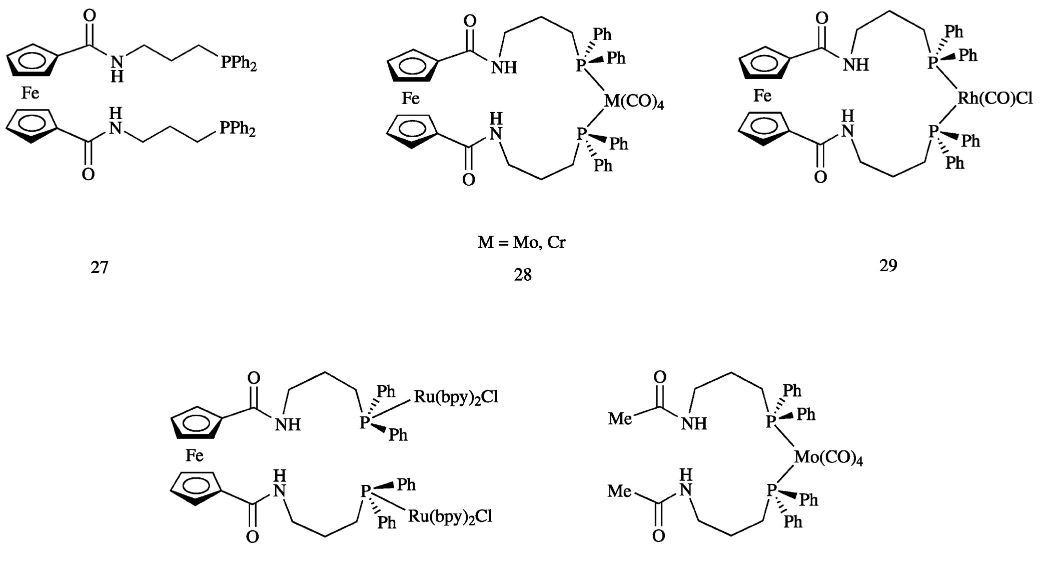


Fig. 10. The α,α,α,α-ferrocene-amide-porphyrin receptor.

plexation in 3:2 CH_2Cl_2/CH_3CN results in cathodic electrochemical perturbations of both the porphyrin and ferrocene redox processes.

Phosphine functionalities have also been fabricated into ferrocene-based receptors with amide functionalities (Fig. 11) [25]. Coordination of the phosphines to a transition metal enhances the strength of anion binding. All receptors electrochemically recognised anions (in 1:1 acetonitrile/dichloromethane) via significant cathodic perturbations of the respective ferrocene and transition metal oxidation wave. The strength of anion binding was greatest with the $Ru(bpy)_2$-substituted receptor **30**, highlighting the importance of favourable electrostatic attractive forces to the anion recognition process.

Astruc and co-workers have produced dendrimers containing up to eighteen ferrocene units **32**–**34** (Fig. 12), and found evidence for a dendritic effect in the anion recognition process [26]. $H_2PO_4^-$ induces the largest cathodic shifts, from 110 mV for **32** to 315 mV for **34**. It can be seen that as the size of the dendrimer increases, so too does the perturbation caused by a particular anion. Recently, this group has synthesised functionalised gold nanoparticles containing (amidoferrocenyl)alkanethiol (AFAT) ligands **35**, for the purpose of redox recognition of oxoanions. These compare favourably to the dendrimers in terms of selectivity for $H_2PO_4^-$ over HSO_4^-, with $H_2PO_4^-$-induced shifts of



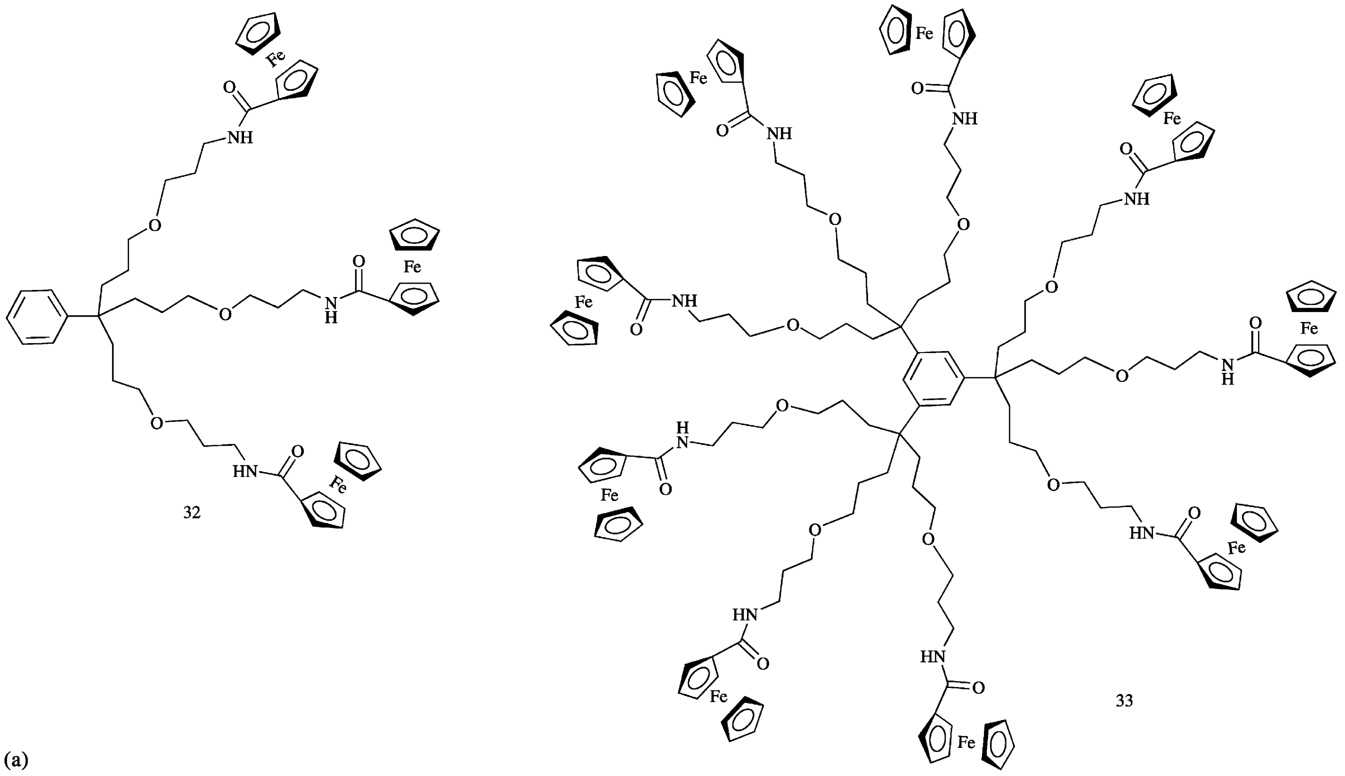
27 28 29 30 31

Fig. 11. Ferrocene-amide phosphine transition metal receptors.

around 200 mV in CH_2Cl_2, and 100–175 mV in the presence of HSO_4^- and Cl^- [27].

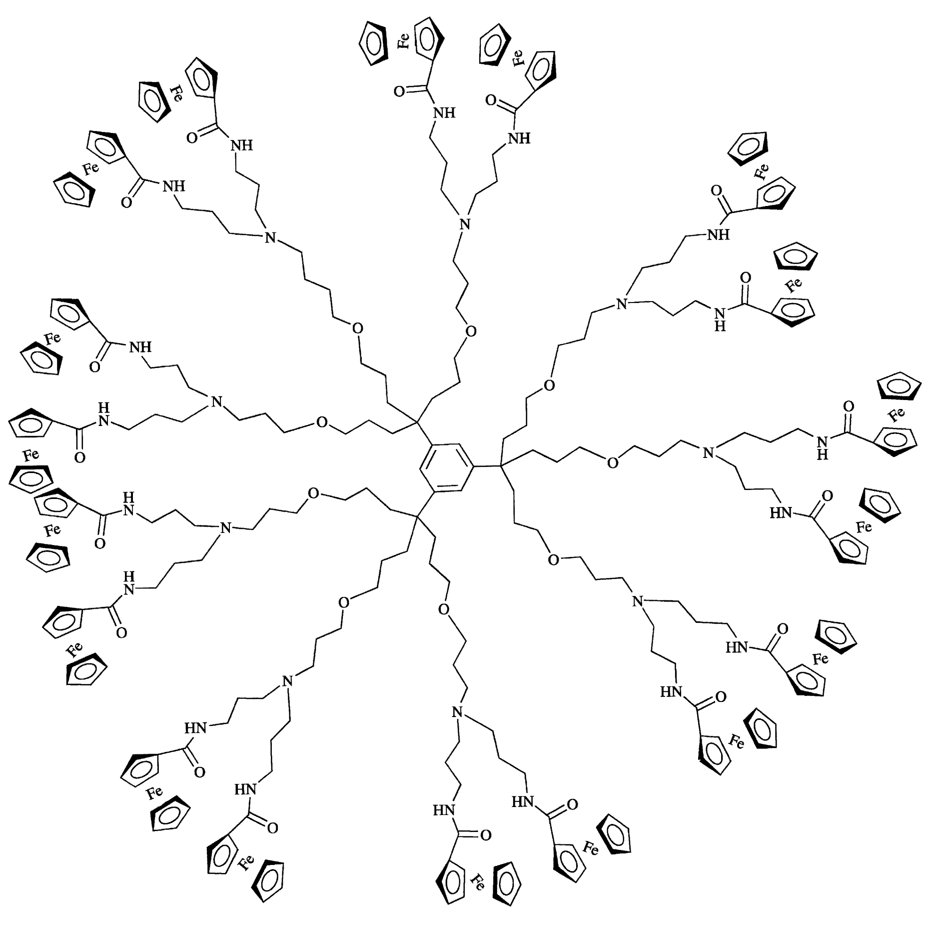
Lower rim poly-ferrocene substituted calixarenes (Fig. 13) have also been synthesised, and shown to electrochemically sense Cl^-, HSO_4^- and $H_2PO_4^-$ anions in CH_2Cl_2, with shifts of up to 160 mV being observed with $H_2PO_4^-$ [28].

Receptors capable of operating under aqueous conditions are obviously important, given the prevalence of anions in biological and environmental systems. However, the large hydration energies of anions make their sensing in water a challenging task [9]. Beer et al. have synthesised a series of acyclic and cyclic ferroceneamine ligands as shown in Fig. 14. These have been shown to



(a) 32 33

Fig. 12. Astruc's ferrocene dendrimers.



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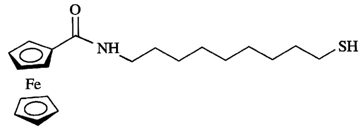


(b) 35

Fig. 12 (*Continued*)

selectively bind and electrochemically sense phosphate and sulphate as well as nucleotide ions in aqueous solution [29–31].

In general, the selectivity of these receptors is dependent upon pH. ^{31}P-NMR showed that receptors **36**, **37** and **38** bind adenosine triphosphate and hydrogenphosphate in water. At pH 6.5, where at least two of the nitrogen atoms are protonated, 1:1 complexes were formed. Electrochemical experiments at the same pH showed cathodic shifts with the phosphate anions of 60–80 mV. Receptor **39** discriminates for sulphate over phosphate at pH 4 in 70:30 THF/H_2O, with cathodic shifts of 54 and <10 mV, respectively. Compound **40** shows shifts of 23 mV with sulphate at pH 4, and 30 mV with phosphate at pH 8.

Molecule **37** shows a perturbation of the Fc^{+}–Fc redox couple by 50 mV upon addition of phosphate at pH 7 in water. Sulphate on the other hand results in a negligible shift. Calibration curves of the change in the half-wave potential $\Delta E_{1/2}$ versus the $[A^{-}]/[L]$ ratio at a certain pH value showed that the concentrations of phosphate and sulphate in the presence of competing anions can be quantitatively determined using receptors **37** and **39**. This demonstrates their potential for use as prototype anion sensors. The ferrocene-appended guanidinium receptor **41** senses pyrophosphate in methanol/water mixtures, exhibiting cathodic shifts of up to 70 mV [32].

A range of receptors **42**–**46** (Fig. 15) has also been synthesised in which both open chain and cyclic polyaza

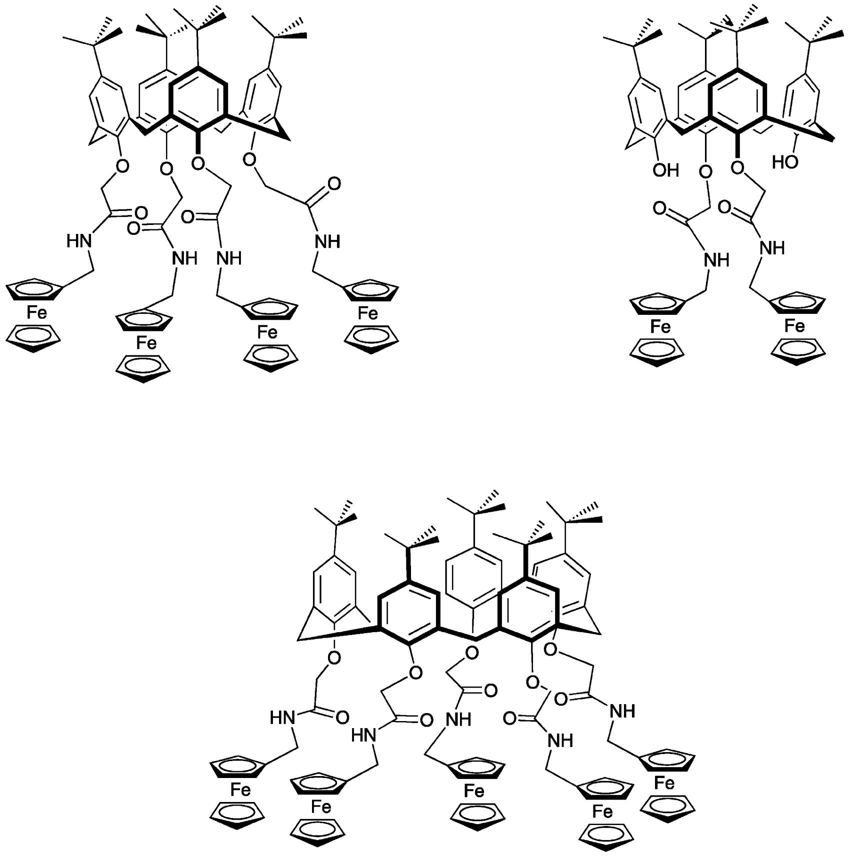


Fig. 13. Lower-rim calixarene ferrocene receptors.

and aza–oxo compounds have a varying number of ferrocene groups attached [33]. Electrochemical measurements in aqueous solution show cathodic shifts of 30–40 mV with ATP and phosphate. Measurements in acetonitrile show a cathodic shift of up to 200 mV upon addition of $H_2PO_4^-$.

Aza-macrocycles functionalised with ferrocene arms (Fig. 16) have also been shown to possess anion binding properties. Receptors **47**–**50** [31,34] are capable of electrochemically detecting sulphates, phosphates and ATP in 70:30 THF/H_2O solutions. Also, receptor **51** has been shown to electrochemically recognise both chloride and benzoate anions in MeCN/CH_2Cl_2 solutions, with shifts of 30–50 mV [35].

Shinkai and coworkers have reported that ferroceneboronic acid (**52**) (Fig. 17) acts as an electrochemical

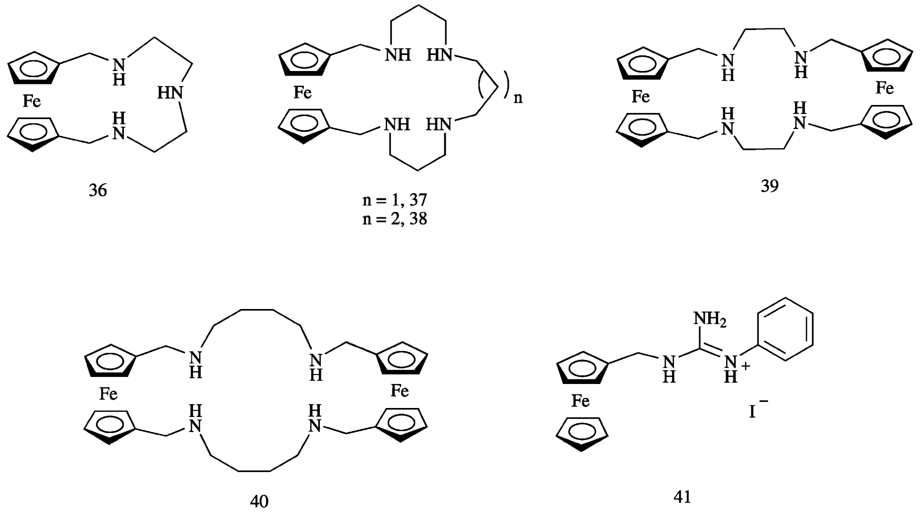


Fig. 14. Examples of water soluble ferrocene-amine receptors.

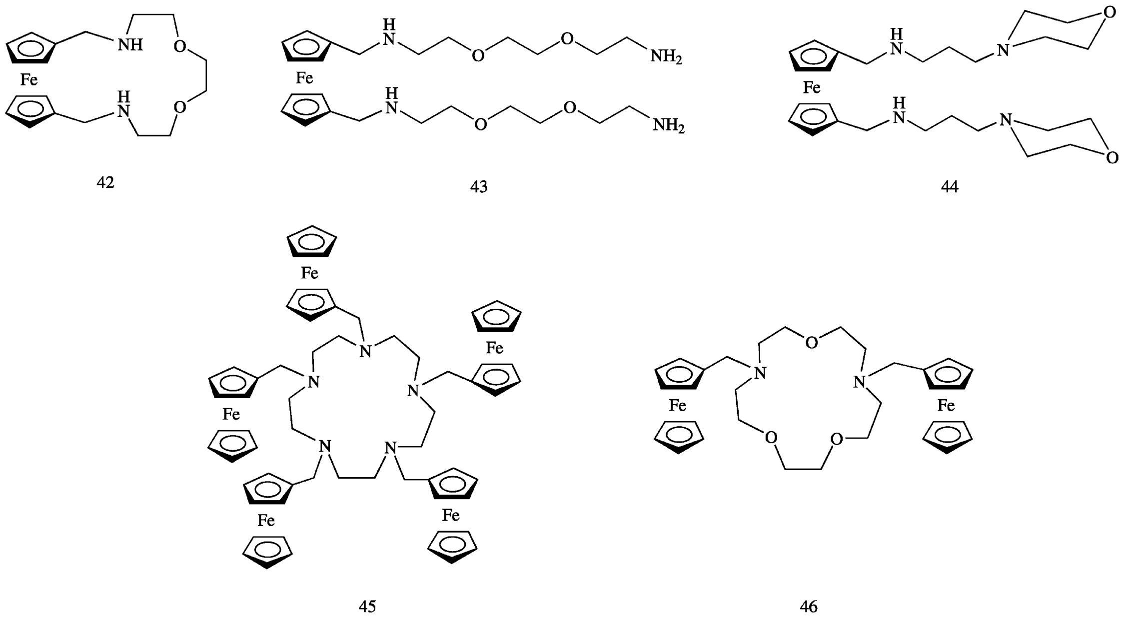


Fig. 15. Polyaza and aza–oxo ferrocene receptors.

anion sensor [36]. It exhibits excellent selectivity for fluoride ions in the presence of other halides and anions such as SCN$^-$, SO$_4^{2-}$ and H$_2$PO$_4^-$. A K_{ox} value of 1000 M^{-1} in MeOH/H$_2$O was found for fluoride, compared with values of less than 2 M^{-1} for chloride and bromide. The fluoride ion is a hard base, and therefore, interacts considerably with the hard boron atom. Oxidation results in the ferrocene group becoming more electron-withdrawing. The electron density of the boron atom decreases, and therefore, the strength of the fluoride complex increases. Chiral ferrocenylboronic acids with intramolecular tertiary amine groups are capable of binding saccharides at neutral pH [37]. Binding can also be detected visually by the redox reaction between ferrocenylboronic acid derivatives and certain dyes [38].

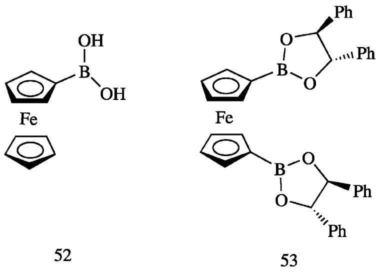


Fig. 17. Ferroceneboronic acid receptors.

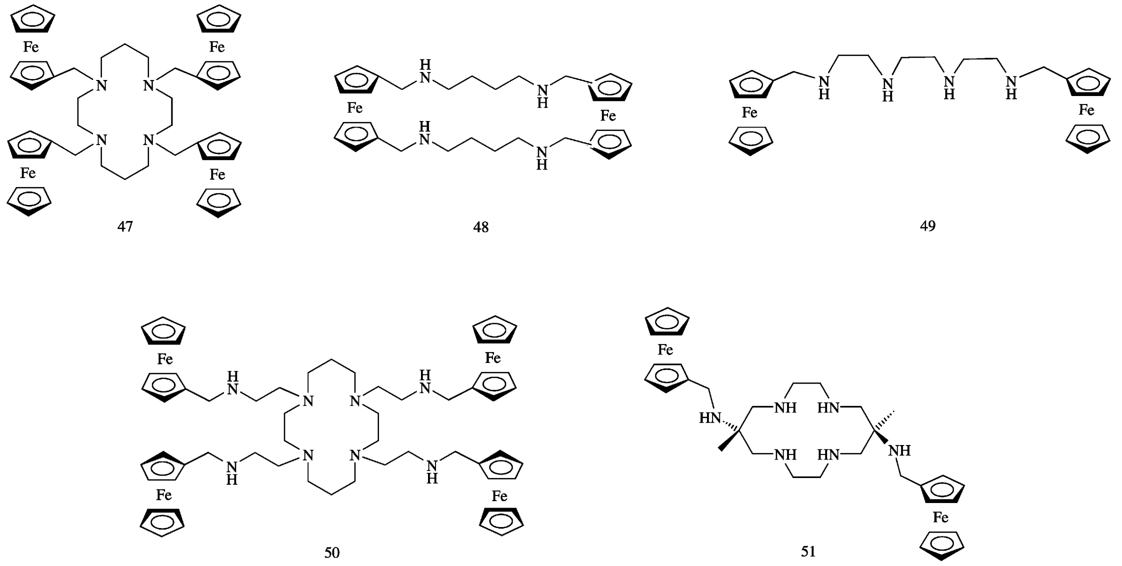


Fig. 16. Ferrocene-functionalised aza-macrocycles.

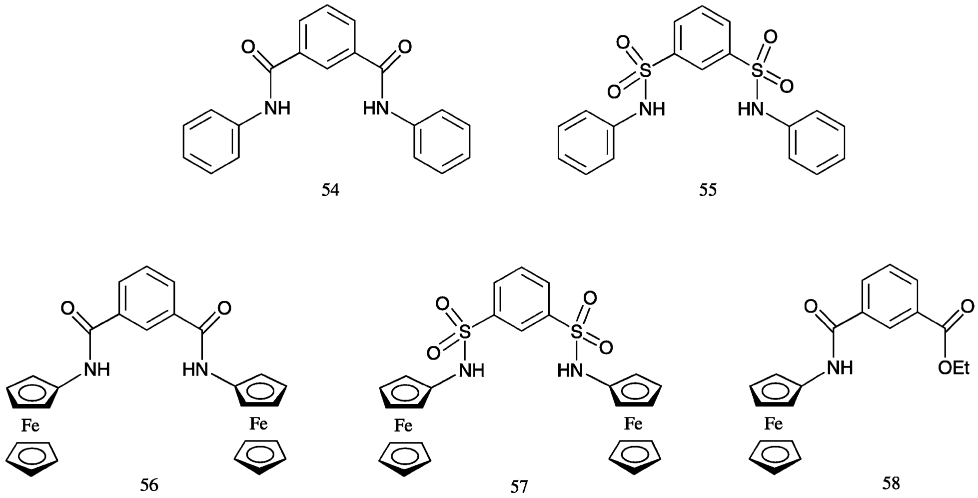
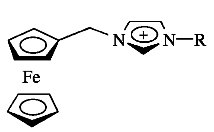


Fig. 18. Isophthalimide and disulphonamide receptors.



59 R = Me
60 R = Et
61 R = Pr
62 R = Bu
63 R = $FcCH_2$

Fig. 19. Ferrocenyl imidazolium salt anion receptors.

A bidentate bis(boronate) Lewis acid **53** (Fig. 17) also acts as a fluoride sensor. Reaction with two or more equivalents of fluoride in $CHCl_3$ or CH_2Cl_2 under aerobic conditions leads to a colour change from orange to pale green. No colour change is observed under anaerobic conditions, or in the presence of other common anions. It is proposed that F^- initially complexes to both boron centres, and subsequently renders the iron centre open to aerobic oxidation. A 146 mV anodic shift in the oxidation potential of the iron centre is observed in the presence of fluoride [39].

Crabtree and coworkers have investigated the anion-binding properties of isophthalimide (**54**) and disulphonamide (**55**) receptors [40,41], and have extended this further with the incorporation of ferrocene subunits, as shown in Fig. 18 [42]. Addition of Cl^- anions to CD_2Cl_2 solutions of **56** and **57** resulted in large chemical shift changes, up to 3.13 ppm for the amide N–H proton of **57**. The stability constant for **57** was found to be 9500 M^{-1}, whereas that for the monamide **58** was only 30 M^{-1}, demonstrating the importance of the two convergent hydrogen-bonding groups. Disappointingly, relatively low cathodic electrochemical shifts of 20 and < 5 mV were observed for **57** and **58**, respectively, after addition of one equivalent of Cl^-.

A new class of anion receptors includes the ferrocenyl imidazolium salts as synthesised by Howarth and coworkers and shown in Fig. 19 [43]. Addition of Cl^-, Br^-, I^-, NO_3^- and HSO_4^- to $CDCl_3$ solutions of **63** resulted in significant downfield shifts of the H-2 proton of the imidazolium ring, accompanied by signal broadening. Similar results were obtained with receptors **59**–**62**, with 1:2 receptor:halide binding stoichiometry, and 1:1 with NO_3^- and HSO_4^-. Electrochemical studies are currently being undertaken.

Much research has been done into the anion binding properties of calix[4]pyrroles and their derivatives [44,45]. One recent derivatisation involves a ferrocene group appended to one of the *meso*-positions, as shown in Fig. 20 [46]. Proton NMR studies of **64** in 9:1 CD_3CN/DMSO-d_6 show binding of fluoride, chloride and dihydrogenphosphate. Electrochemical measurements show cathodic shifts of up to 100 mV with $H_2PO_4^-$.

Steed and coworkers have synthesised a series of 'venus flytrap' anion sensors (Fig. 21), based on podands with a hexa-substituted core and arms with hydrogen-bonding and cationic pyridinium groups, with ferrocene attached to the pyridinium **65** [47]. The host is preorganised into a cone conformation, and shows considerable affinity for halides, and chloride in particular, with complexation-induced chemical shifts of up to 1.54 ppm for the NH protons in CD_3CN. The selecitivity trend is $Cl^- > Br^- > I^-$, and some selectivity is also shown for acetate. Preliminary electrochemical studies suggest relatively poor coupling between

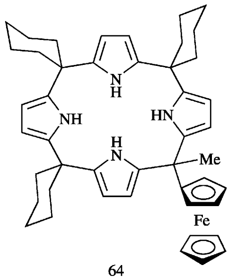


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Fig. 20. Ferrocene–calix[4]pyrrole.

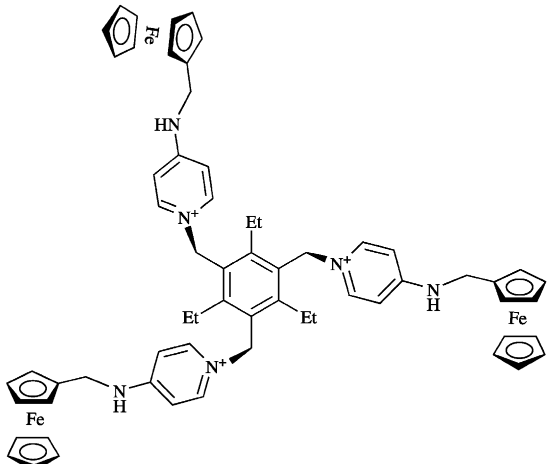

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Fig. 21. ‘Venus flytrap’ anion sensor.

binding and signalling moieties, but the observed selectivity sequence is in agreement with that obtained by NMR.

2.3. Arene and other organometallic receptors

Atwood and coworkers have made considerable progress in the synthesis of new anion hosts by directly attaching cationic metal ions to the calixarene aromatic rings [48]. They have used this approach to synthesise $[CpFe(arene)]^+$ derivatised cyclotriveratrylenes such as **66**, which binds halides and PF_6^- even in the absence of a hydrogen-bonding group such as the amides in **23** and **24**. The upper rim charge preorganisation allows anion binding within the host cavity [49].

Beer and coworkers have made several simple receptors by substituting one cyclopentadienyl ring of a ferrocene with a benzene ring, to give the amide arene CpFe **67** in Fig. 22. The same paper also describes the synthesis of the amide arene tricarbonyl chromium compound **68** [50]. Downfield shifts of the amide N–H protons are observed for both receptors upon addition of chloride or bromide in CD_3CN. For instance, with chloride receptor **67** exhibits a shift of 2.5 ppm, and **68** a shift of 0.9 ppm. Negligible shifts are observed with both unsubstituted metallocene, and the non-metallated aromatic molecule.

Astruc has also used different metallocenes, having synthesised a cationic metallodendrimer with **24** $[CpFe(\eta^6\text{-}N\text{-alkylaniline})]^+$ termini. This molecule is capable of recognising chloride and bromide [51].

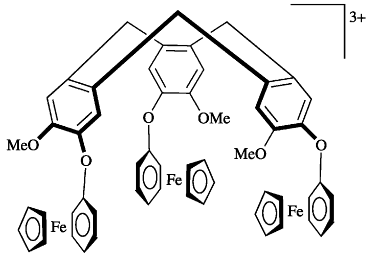
Gale and coworkers have synthesised receptor **69** in Fig. 22 [52] based on the isophthalamide subunit of Crabtree [40,41]. Electron withdrawing $Cr(CO)_3$ groups were attached in order to increase the acidity of the NH protons [42]. ^{1}H-NMR titrations with **80** in CD_3CN showed a selectivity for chloride over other anionic guests, with a log K value of greater than 4. Selectivity for chloride over dihydrogen phosphate is high, perhaps reflecting the steric bulk of the $Cr(CO)_3$ moieties, which may hinder the approach of the bulky $H_2PO_4^-$ to the amide cleft.

3. Optical sensors for anions

Fluorescent techniques exhibit high selectivity in the sensing of target guest species. There has, therefore, been immense interest in the covalent attachment of organic and inorganic luminophores to guest-recognition sites [53]. For example, the anthracene fluorophore has been combined with polyammonium [54], guanidinium [55], zinc(II) amine [56] and calixpyrrole anion recognition sites [57]. Cyclen-appended phenanthridinium lanthanide complexes have been shown to sense halide and hydroxide ions in water [58,59]. Similar lanthanide cyclen complex systems have been shown to bind oxy-anions in aqueous solution [60,61].

3.1. Ruthenium(II)- and rhenium(I)-bipyridyl-based receptors

One of the most extensively investigated systems has been tris(2,2′-bipyridyl)ruthenium(II) ($[Ru(bpy)_3]^{2+}$), which is popular due to its chemical stability, redox properties, excited-state reactivity, and luminescent emission [62,63]. Beer and coworkers have incorporated this moiety into acyclic, macrocyclic and calix[4]arene structural frameworks to produce a new class of anion receptor capable of optical and electrochemical sensing (shown in Fig. 23) [64–66]. The single crystal X-ray



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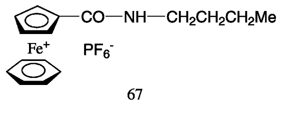

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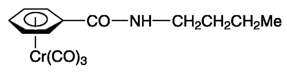

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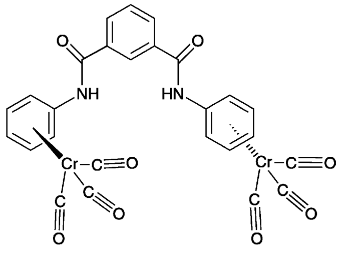


69

Fig. 22. Other metallocene-based receptors.

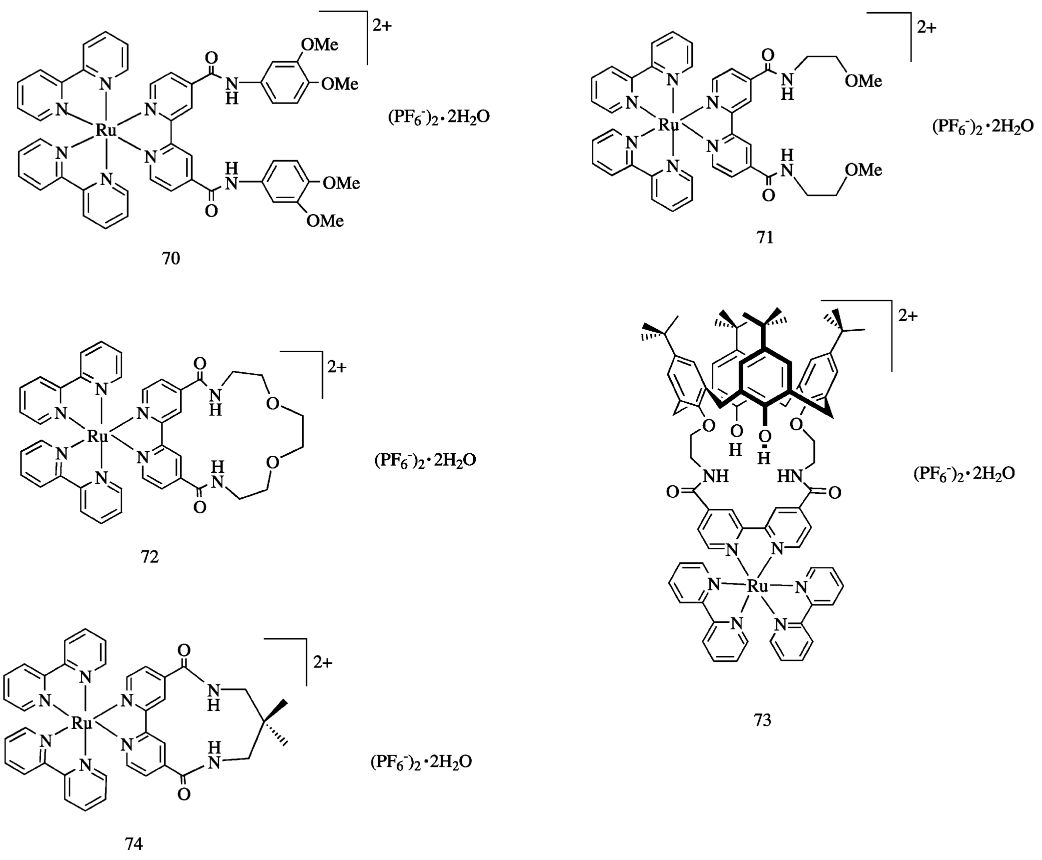


Fig. 23. Ruthenium(II) bipyridyl receptors.

structure of the chloride complex of **70** demonstrates the importance of hydrogen bonding to the anion-binding process (Fig. 24). Stability constants measured in DMSO show the acyclic receptors **70** and **71** to form

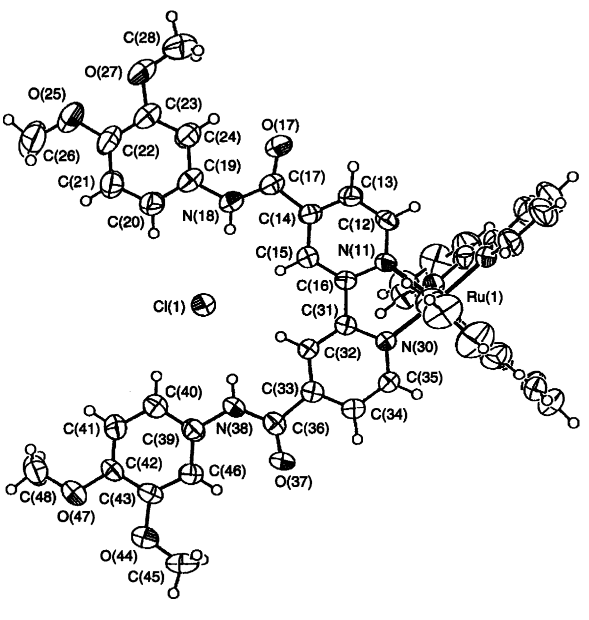
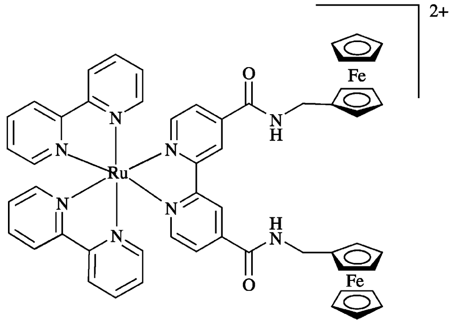


Fig. 24. Single crystal X-ray structures of the chloride complex of **70**. Reproduced with permission from [64]. Copyright 1996, American Chemical Society.

strong complexes with both Cl^- and $H_2PO_4^-$ anions. Receptors **72**–**74** on the other hand form highly selective and thermodynamically stable complexes with $H_2PO_4^-$ ions. Electrochemical studies showed substantial anion-induced cathodic perturbation of the ligand centred amide substituted 2,2′-bipyridine reduction redox couple. These shifts correlated with the stability constant values, with **73** sensing $H_2PO_4^-$ ions in the presence of a 10-fold excess of HSO_4^- and Cl^- ions. Luminescence emission measurements showed all receptors to exhibit a significant blue shift in the MLCT emission band λ_{max} on addition of Cl^- and $H_2PO_4^-$. Receptor **73** displayed the largest perturbation of 16 nm. These shifts were not observed with unfunctionalised $[Ru(bpy)_3]^{2+}$. All shifts were accompanied by a large increase in emission intensity, and it was proposed that this might be due to the bound anion rigidifying the receptor and inhibiting vibrational and rotational relaxation modes of nonradiative decay.

An acyclic $[Ru(bpy)_3]^{2+}$-ferrocene receptor **75** (Fig. 25) has also been prepared [67]. The ferrocene units quench the emission of the ruthenium centre in the free receptor, but addition of $H_2PO_4^-$ ions increases the emission by 20-fold in acetonitrile. This increase is not observed with Cl^- or HSO_4^- ions. Competition experiments in the presence of these anions gives rise to an



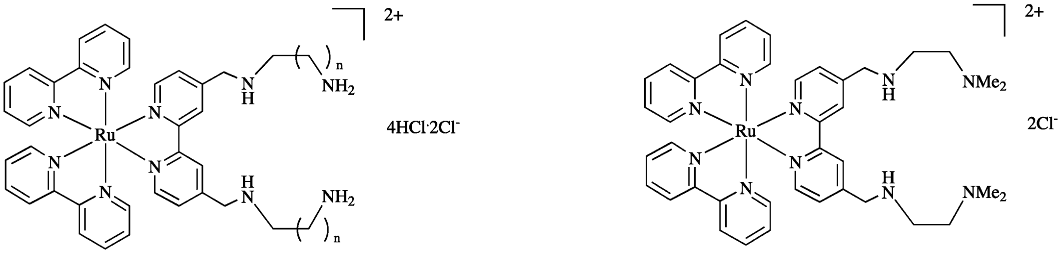
75

Fig. 25. Acyclic $[Ru(bpy)_3]^{2+}$-ferrocene receptor.

emission increase identical to that obtained upon addition of $H_2PO_4^-$. Receptor **75** can, therefore, be considered a $H_2PO_4^-$-selective luminescent anion receptor. The acyclic water soluble ruthenium(II) bipyridyl polyaza receptors **76–79** (Fig. 26) have been shown to bind and detect phosphate anions in aqueous media by MLCT luminescent emission quenching [68].

Other mixed-metal receptors include cleft-type molecules (Fig. 27), in which d^6 metals Ru^{II}, Os^{II} and Re^I were used, with a variety of different bridging groups [69]. These also exhibit selectivity for $H_2PO_4^-$ over chloride. The bridging unit has a considerable effect on the strength of binding. For instance, a *meta*-phenylene-bridged ligand gives a stability constant with dihydrogen phosphate in DMSO of 55 M^{-1}. The *para* analogue results in a binding constant of 4320 M^{-1}. The Os^{II} receptors exhibited larger anion stability constants, due to the efficient Lewis-acidic character of the $[Os(bpy)_3]^{2+}$ moiety. The mixed Re^I–Pd^{II} metal macrocycle in Fig. 28 binds perchlorate anion, which can be detected via MLCT enhancement in acetone [70].

Particularly noteworthy are the receptors **80–82** (Fig. 29), synthesised by Beer and coworkers, which exhibit a marked selectivity for chloride ions [71]. Extremely stable 1:1 complexes are formed in DMSO, with stability constants of up to 4×10^{-4} M^{-1}. ^1H- and ^{31}P-NMR shows no evidence of $H_2PO_4^-$ binding. Luminescence studies show a blue-shift of the MLCT emission band with significant intensity enhancement in response to the addition of chloride anions (Fig. 30), but no response to $H_2PO_4^-$. The rigidity of the macrocycle is thought to



76, n = 1
77, n = 2
78, n = 3

79

Fig. 26. Water soluble ruthenium(II) bipyridyl polyaza receptors.

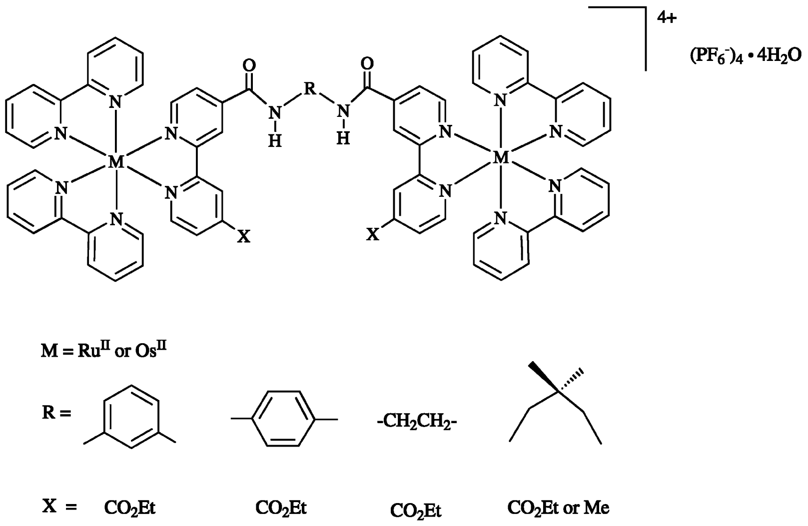


Fig. 27. Cleft-type mixed-metal receptors.

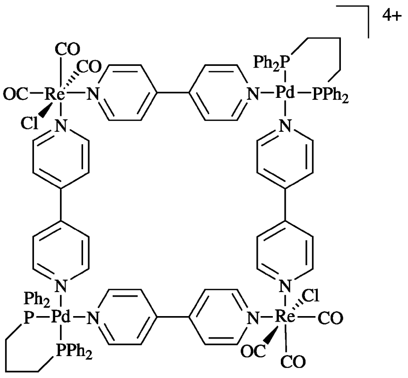


Fig. 28. Rhenium(I)–Palladium(II) macrocycle.

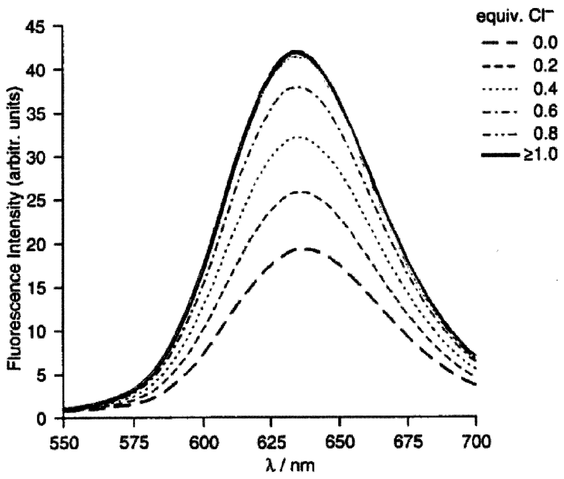


Fig. 30. Fluorescence emission spectra of **81** in acetonitrile with addition of chloride [*Chem. Commun.* (1995) 2245]. Reproduced by permission of The Royal Society of Chemistry.

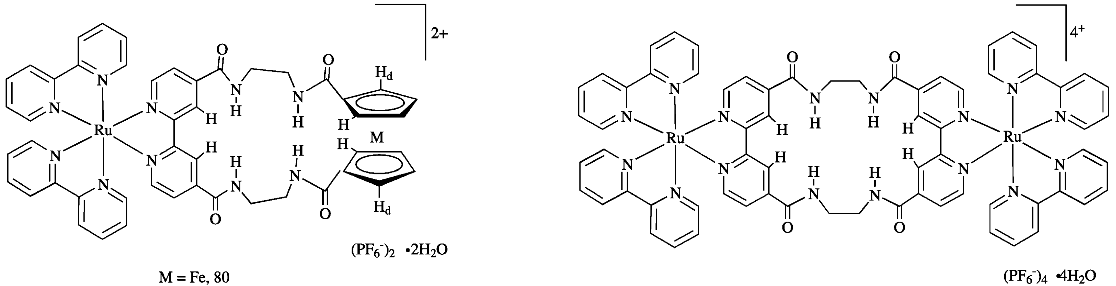
contribute to this selectivity, since acyclic analogues tend to prefer $H_2PO_4^-$. The larger size and tetrahedral shape of this anion make it incompatible with the macrocycle's cavity. However, increasing the size of the cavity by two or four methylene units dramatically reverses the trend in anion selectivity.

The $[Ru(bpy)_3]^{2+}$ moiety has also been utilised by Deetz and Smith, who have attached saccharide-binding boronic acid groups, as in molecule **83** (Fig. 31(a)) [72]. The phosphate group of the sugar is presumably bound to the amide protons in the cleft, while the boronic acid groups coordinate to the sugar. The presence of the phosphorylated sugars in aqueous solution is detected by perturbations in the luminescent properties of the complex. Rhenium analogues of this material have previously been used to bind simple sugars [73].

Watanabe and coworkers have produced imidazole-functionalised $[Ru(bpy)_3]^{2+}$ complexes such as **84** (Fig. 31(b)) [74]. These recognise anionic and neutral phosphodiesters with luminescent signal enhancement observed in acetone. The receptor is proposed to form 1:1 complexes with tetraethylammonium diphenyl phosphate (TDPP) or dibenzylphosphate (DBHP).

Ruthenium(II)- and rhenium(I)-bipyridylcalix[4]diquinone receptors **85** and **86** (Fig. 32) selectively bind and sense acetate ions [68,75]. Addition of acetate to acetonitrile solutions of **85** resulted in a 500% increase in the emission intensity, suggesting that anion complexation inhibits the intramolecular oxidative electron transfer quenching mechanism between the ruthenium(II)-bipyridyl and calix[4]diquinone centres.

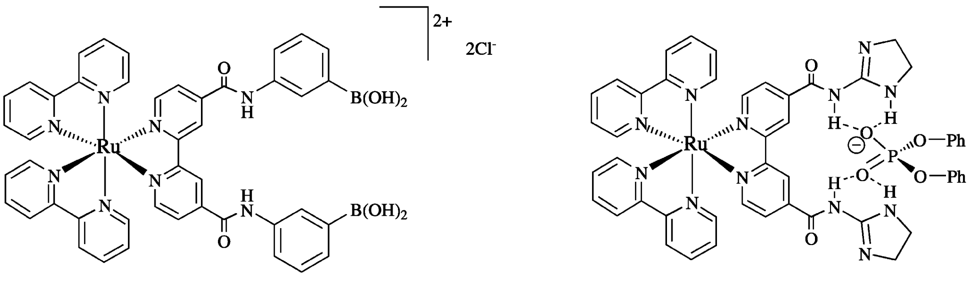
A range of ruthenium receptors bearing 5,5′-amide substituents has been synthesised (Fig. 33) [76]. It has been shown that the selectivity of these molecules is dependent on the amide substituent and solvation factors. Anion binding was generally signified by decreases in the absorbance and hypsochromic shifts for the MLCT and LC bands at ca. 260 and 300 nm, respectively. In 9:1 and 7:3 CH_2Cl_2/MeOH, all receptors display the selectivity sequence $Cl^- > NO_3^- > AcO^-$. This suggests that chloride provides the best match for the binding site. Receptors **87** and **88** remain selective for chloride in 1:1 CH_2Cl_2/MeOH while hosts **89** and **90** become selective for nitrate. These receptors possess large, lipophilic substituents that can partially shield the amide binding site from the surrounding solvent. The anion must undergo significant desolvation before binding can occur, and so the selectivity trend reflects the hydration energies $AcO^- > Cl^- > NO_3^-$. Receptors **87** and **88** have smaller amide substituents and so the anion desolvation does not dictate the selectivity sequence, leaving the geometric complementarity as dominant. Investigations are currently underway into the enantioselective recognition of anionic guest species



M = Fe, 80
M = Co⁺, 81

82

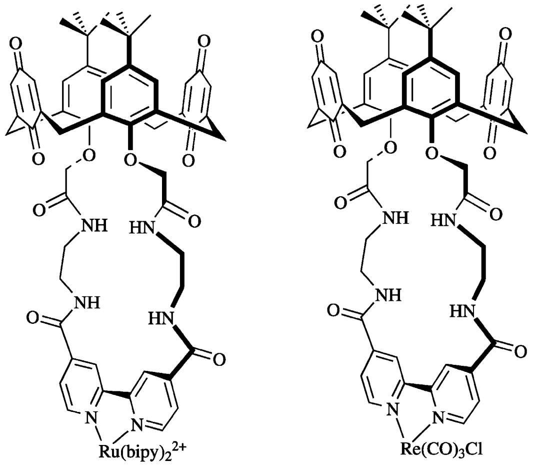
Fig. 29. Macrocyclic halide-selective receptors.



83
(a)

84
(b)

Fig. 31. (a) $[Ru(bpy)_3]^{2+}$-boronic acid. (b) Imidazole-functionalised $[Ru(bpy)_3]^{2+}$ +TDPP.



85
86

Fig. 32. Ruthenium(II)- and rhenium(II)-bipyridylcalix[4]diquinone receptors.

using chiral receptors based on similar systems with both ruthenium(II) and rhenium(I) [77].

Ruthenium and rhenium bipyridyl complexes have been utilised in the synthesis of ion-pair receptors. Using a similar approach to that of the cobaltocenium receptor **11**, crown ether molecules have been attached to a rhenium(I) amide bipyridine architecture (Fig. 34) [78,79]. ^{1}H-NMR studies in 1:1 CD_3CN/DMSO-d_6 (Table 2) showed all receptors to be selective for acetate over chloride, with downfield shifts of the bpy protons indicative of hydrogen bonding. Titrations in the presence of potassium cations revealed a positive cooperative effect, with increases in binding constants of 80–115% for **91** and **93**, and 40–50% for **92** and **94**. This effect may be due to the longer *m*-xylyl spacer in **92** and **94**, which reduces the through space electrostatic interaction between cation and anion binding sites. Emission spectroscopic titrations also revealed cooperative binding effects, in particular for receptor **94** with acetate in CH_3CN (Fig. 35). This suggests a preorganisation of the receptor by formation of a K^+ sandwich complex.

Another class of ion-pair receptors involves attachment of a calix[4]arene tetraester cation binding site to rhenium(I) and ruthenium(II) bipyridines (Fig. 36) [80]. These molecules bind alkali metal (Li^+, Na^+)-halide (Br^-, I^-) ion pair species. Proton NMR titrations reveal that the presence of a lower-rim bound cation greatly enhances anion binding, with an increase of up to 60-fold observed with **98**. Halide binding enhancement is greater with the neutral rhenium(I) receptors **95**–**98** than for the charged ruthenium receptors **99**–**102**, which may be due to unfavourable electrostatic effects.

3.2. Other optical sensors

Despite being widespread, ruthenium(II) and rhenium(I) 5,5′-bipyridyl receptors are by no means the

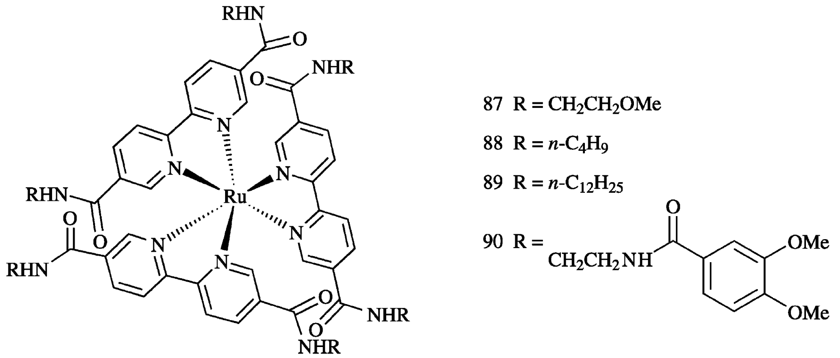
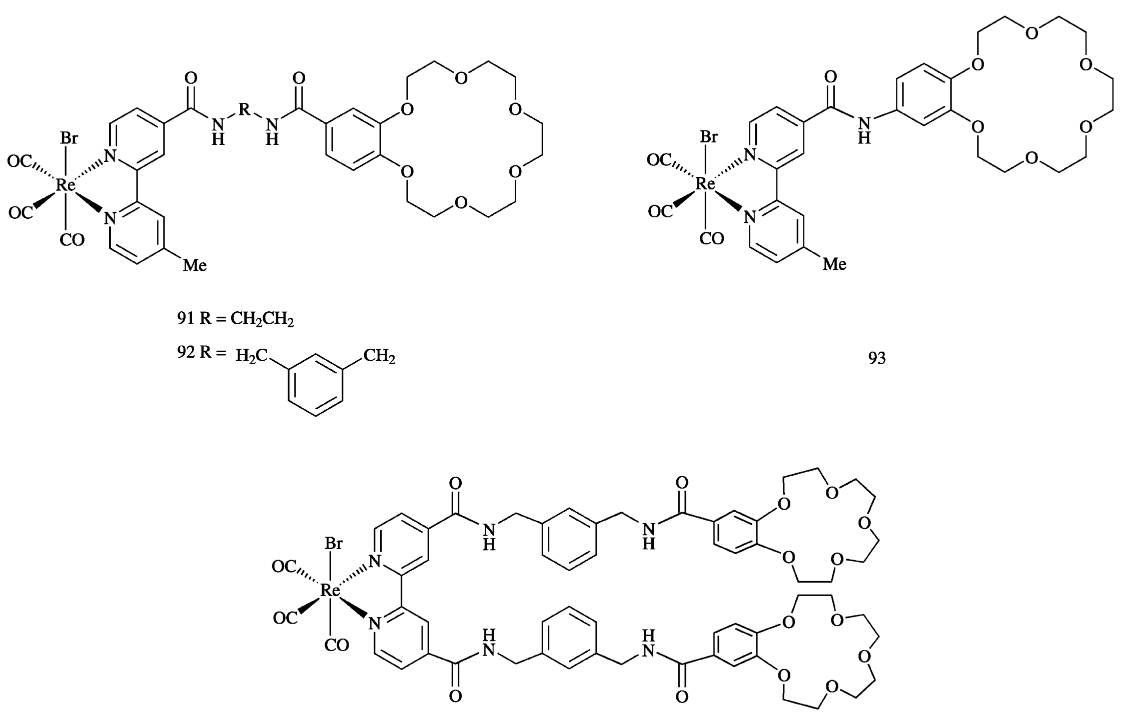


Fig. 33. Ruthenium receptors bearing amide substituents.



94

Fig. 34. Rhenium(I) bipyridine crown ether ion-pair receptors.

only form of transition metal-containing optical anion sensor. Several different metals and ligand systems have been investigated.

Williams and Goodall have made the isomeric bis-terpyridine complexes of iridium(III) shown in Fig. 37 [81]. Addition of chloride anion quenches the luminescence in aqueous solutions. Receptor **104** is sensitive to chloride at physiologically relevant concentrations. Other halides also quench the luminescence efficiently, but other anions, including $H_2PO_4^-$, NO_3^- and SO_4^{2-} have no effect.

Table 2
Stability constants for acetate and chloride binding of **91**–**94** in the presence and absence of 1 equivalent of KSCN in 1:1 CD_3CN/DMSO-d_6

Receptor	K (M^{-1}) [a]			
	AcO^-	AcO^- (K^+)	Cl^-	Cl^- (K^+)
91 (NH)	375	527	63	113
91 (H3)	371	560	62	117
92 (NH)	98	92	27	40
92 (H3)	101	94	27	40
93 (NH)	[b]	[b]	34	73
93 (H3)	209	314	35	74
94 (NH)	623	546	65	91
94 (H3)	661	540	73	107

[a] K determined from the change in chemical shift of the bpyNH and bpyH3 protons; errors $\leq 7\%$.

[b] BpyNH becomes too broad on anion addition to determine K with accuracy.

Lees and coworkers have synthesised a series of heterometallic cyclophanes with both octahedral and square planar metal components (Fig. 38) [82]. Molecules **105**–**109** were studied with a variety of anions, including ClO_4^-, OAc^-, OTf^-, PF_6^- and BF_4^-. Only PF_6^- and BF_4^- induced changes in the luminescence in acetone. Luminescence intensity initially decreased by a small amount, followed by an increase to a plateau.

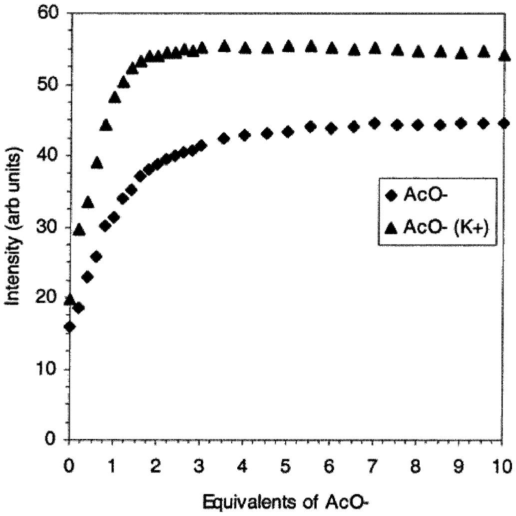
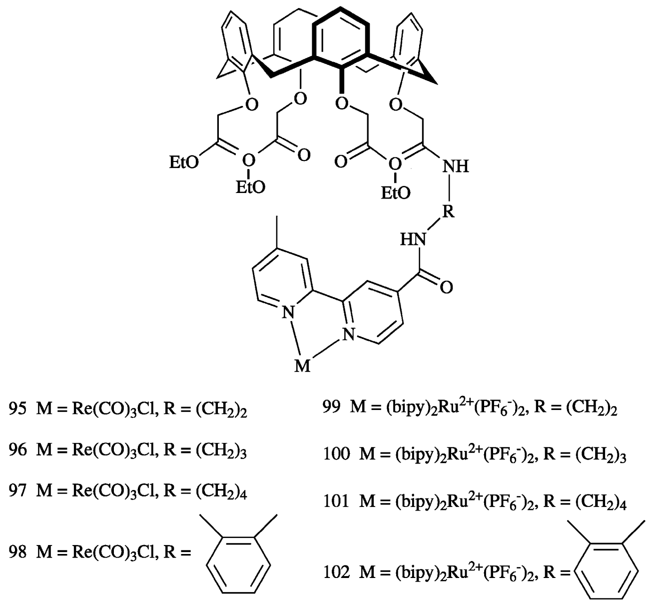


Fig. 35. Binding curves for receptor **94** and TBAOAc in CH_3CN, in the presence and absence of 1 equivalent of KSCN (Shown for the emission response at 600 nm). Reproduced with permission from [79] (p. 2869). Copyright 2001, American Chemical Society.

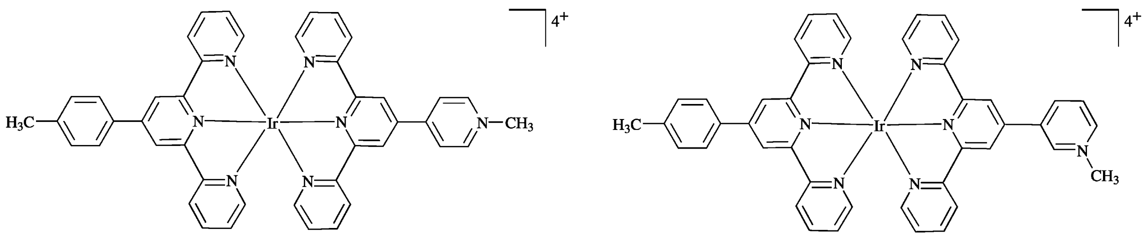


95 M = $Re(CO)_3Cl$, R = $(CH_2)_2$
96 M = $Re(CO)_3Cl$, R = $(CH_2)_3$
97 M = $Re(CO)_3Cl$, R = $(CH_2)_4$
98 M = $Re(CO)_3Cl$, R =
99 M = $(bipy)_2Ru^{2+}(PF_6^-)_2$, R = $(CH_2)_2$
100 M = $(bipy)_2Ru^{2+}(PF_6^-)_2$, R = $(CH_2)_3$
101 M = $(bipy)_2Ru^{2+}(PF_6^-)_2$, R = $(CH_2)_4$
102 M = $(bipy)_2Ru^{2+}(PF_6^-)_2$, R =

Fig. 36. Rhenium(I) and ruthenium(II) bipyridyl calix[4]arene receptors.

Sessler and coworkers have recently synthesised phenanthroline complexes bearing fused dipyrrolylquinoxaline anion recognition sites (Fig. 39) [83]. These molecules possess electron-withdrawing moieties that render the pyrrole N–H protons more acidic, and thereby, enhance anion-binding affinities. Both **110** and **111** showed considerable affinity for fluoride in DMSO, with association constants of 12 000 and 54 000 M^{-1}, respectively, and values of 50 or less with chloride and dihydrogenphosphate.

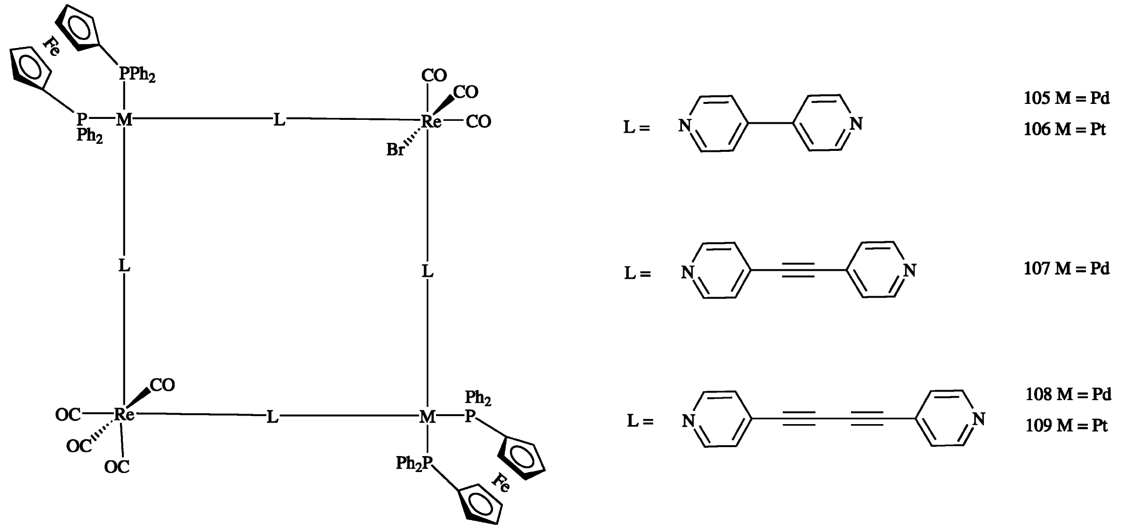
An increasingly common tactic in receptor design is to use a transition metal to coordinate the anion. Fabbrizzi and coworkers have synthesised the tripodal amino ligands in Fig. 40. Design strategy is such that one or two vacant coordination sites remain on the metal ion for the anion, and some sort of functionality can be introduced to affect selectivity, or to impart signalling capability. The zinc complex of **112** binds aromatic anions such as 4-*N*,*N*-dimethylaminebenzoate in ethanol, with progressive quenching of the anthracene fluorescent emission, and complete quenching with a 1:1 sensor/analyte ratio [84]. The log *K* value for the association equilibrium is 5.45. The zinc complex of **113** gives stable 1:1 adducts with carboxylate anions in methanol, with log *K* values ranging from 4 to 5. Only carboxylates bearing an aromatic substituent quench the emission of the ligand [85]. Similar systems have been used for the sensing of amino acids [86].



103

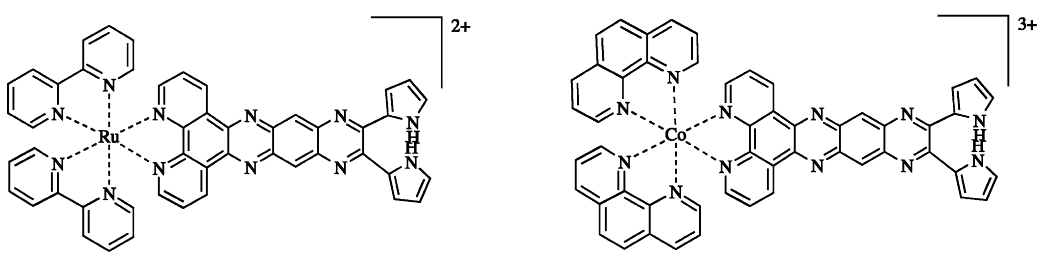
104

Fig. 37. Iridium(III) based receptors.



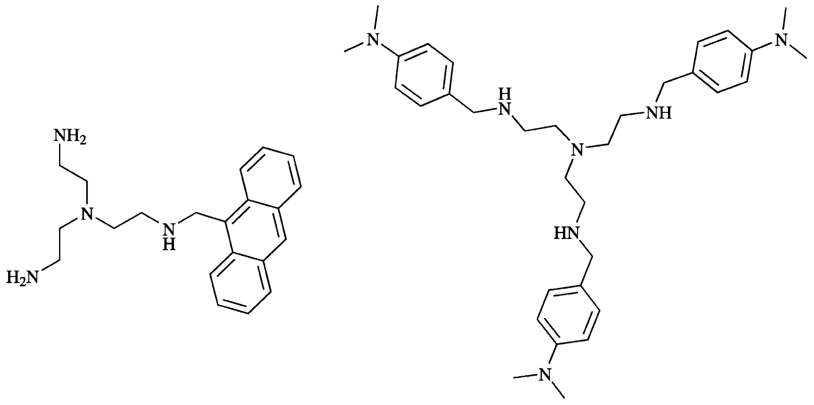
105 M = Pd
106 M = Pt
107 M = Pd
108 M = Pd
109 M = Pt

Fig. 38. Heterometallic cyclophane anion receptors.



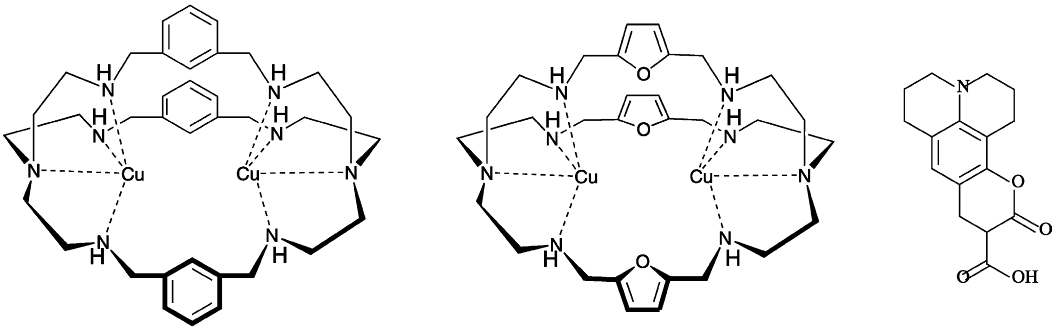
110 **111**

Fig. 39. Phenanthroline complexes with fused dipyrrolylquinoxaline anion recognition sites.



112 113

Fig. 40. Tripodal amino ligands.

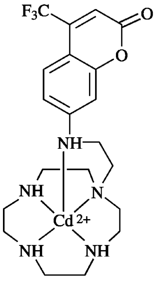


114 115 coumarine 343

Fig. 41. Anion-binding bis-tren cryptands.

This tactic has been extended in the synthesis of bis-tren cryptands which incorporate first two metal ions, and then an ambidentate anion, according to a cascade mechanism [87]. Molecule **114** in Fig. 41 shows a dicopper(II) cryptate with a 1,3-xylyl spacer. When titrated with NaN_3 in aqueous solution, the colour changes from pale blue to bright green, and an anion-to-metal LMCT absorption band appears at 400 nm. The azide fills the empty cage cavity and coordinates in the axial position of each copper. The dimetallic receptor does not recognise the shape of the anion or its electrical charge, but rather its bite length, which is the distance between two consecutive donor atoms. The receptor is relatively rigid, and does not include monoatomic halide anions at all.

The analgous receptor **115** incorporates a 2,5-furanyl spacer, which is relatively flexible. Upon addition of halide ions, the solution changes from pale blue to bright yellow, with the development of an intense band above 400 nm, attributed to the inclusion of the halide ion. Crystal structure analysis of the bromide complex shows the anion encapsulated within the cage, bridging the two trigonal bipyramidal copper centres. A defined selectivity for chloride is evident, although linear triatomic anions such as N_3^- and NCS^- are also bound. The complex seems able to expand and contract its



116

Fig. 42. Cadmium(II) cyclen-coumarin receptor.

cavity in order to encapsulate anions of variable size and shape [88].

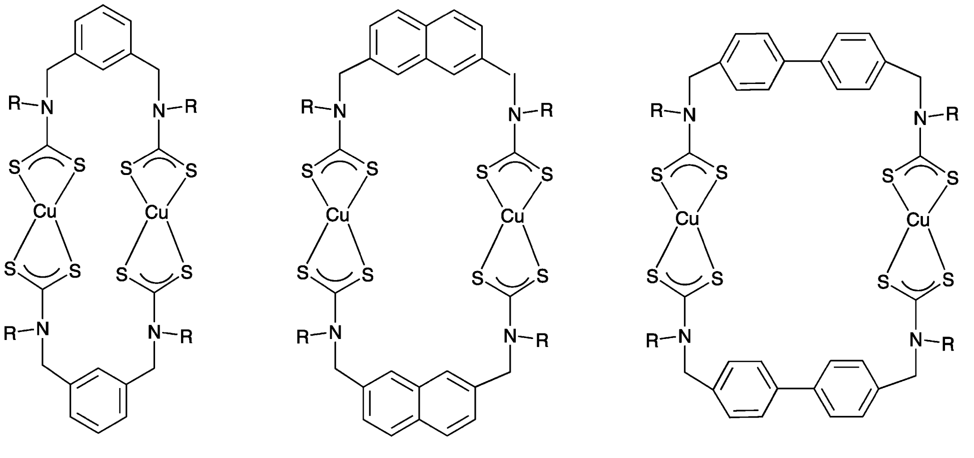
Receptors **114** and **115** generally give rise to only small changes in the absorption spectra, which limits their practical use as molecular sensors. Therefore, a chemosensing ensemble approach has been adopted, using coumarine 343 as a fluorescent indicator [89]. It possesses a carboxylate function capable of bridging the copper(II) centres. Complete quenching was observed upon titration in aqueous solution, with formation of a 1:1 adduct with an association equilibrium constant log K_{ass} of 4.8. The solution can then be backtitrated with anions such as carbonate, azide and cyanate to give complete recovery of coumarine emission.

Kikuchi and coworkers have utilised this strategy in the design of receptor **116** in Fig. 42, which works in neutral aqueous solution [90]. Initially, the cadmium(II) is coordinated by the four nitrogens of cyclen and the aromatic amino group of coumarin. Added anions displace the coumarin from its coordination spot, and in the process, the excitation spectrum is altered. Addition of an excess of pyrophosphate to buffered aqueous solutions resulted in a shift in the excitation spectrum to longer wavelength, from 342 to 383 nm. Citrate also showed high affinity, with apparent dissociation constants K_d being in the region of 10^{-5} M for both of these anions. The binding of pyrophosphate was found to be reversible, with addition of Mg^{2+} resulting in a return to the original excitation spectrum [90].

4. Recent new directions in anion sensing

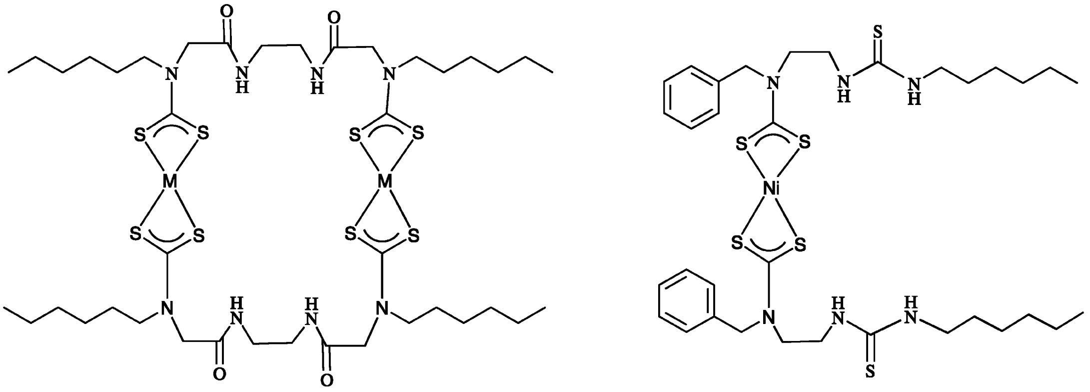
Self-assembled dithiocarbamate–copper(II) macrocycles **117–119** (Fig. 43) have been shown by Beer and coworkers to be capable of electrochemical anion recognition [91]. The naphthyl-based macrocycle **118** shows substantial cathodic shifts in oxidation potential with tetrahedral anions such as dihydrogenphosphate and particularly perrhenate, which results in a cathodic shift of 85 mV. The xylyl-spaced macrocycle **117** exhibits a 20 mV cathodic shift in response to chloride, but little response to other anions. UV–vis spectroscopy and ES-MS studies have further demonstrated the selectivity of **118** for ReO_4^-. Results suggest that the macrocyclic systems exhibit a degree of anion selectivity based upon the macrocycle ring size.

Acyclic and cyclic dithiocarbamate receptors incorporating thiourea and amide hydrogen bond donor groups have also been synthesised, and are shown in Fig. 44 [92]. Proton NMR titrations with **120** in DMSO-d_6 resulted in significant downfield shifts, particularly for the amide protons, of up to 2.1 ppm. UV–vis titrations with **120** and **123** in DMSO showed that **120** strongly complexes acetate in a 1:1 stoichiometry with log β_1 of 5.36, whereas $H_2PO_4^-$ is bound in a 2:1 anion:receptor ratio, with log β_1 of 4.10 and log β_2 of 9.07. **123** also forms strong complexes with carboxylate anions, resulting in log β_1 of 6.13. Electrochemical investigations with **121** in 7:2:1 $CH_3CN/CH_2Cl_2/$DMSO resulted in significant cathodic shifts of the



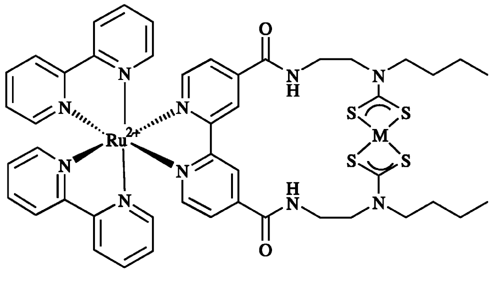
117 118 119

Fig. 43. Dithiocarbamate-Cu(II) anion receptors.



M = Ni, 120
M = Cu, 121
M = Zn, 122

123



M = Ni, 124
M = Zn, 125

Fig. 44. Dithiocarbamate anion receptors with thiourea and amide hydrogen bond donor groups.

$Cu^{II/III}$ oxidation potential by up to 160 mV with $H_2PO_4^-$.

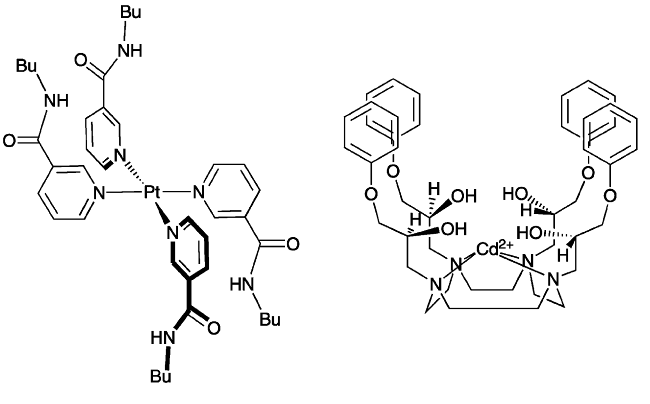
Receptors **124** and **125** add a dithiocarbamate subunit to the well-studied $Ru(bpy)_3^{2+}$ group [92]. **124** shows significant downfield shifts in the ^1H-NMR upon addition of anions, and displays the selectivity trend $Cl^- \sim OAc^- > Br^- \gg I^-$. **124** forms stronger complexes with Cl^- and OAc^- than its acyclic analogue **71**.

Gale and Loeb have used platinum(II) nicotinamide complexes as receptors for oxo-anions [93]. The receptor **126** provides both hydrogen bond donating amides and an electrostatic contribution from the metal centre. X-ray structure analysis shows that the molecule adopts a 1,2-alternate conformation, in which there are two amide hydrogen bonding sites in a *cis* orientation on each side of the metal square plane. ^1H-NMR spectroscopic titrations show the receptor capable of binding a range of oxo-anions, with a particular selectivity for the planar bidentate anions NO_3^- and AcO^-. These are bound in a 1:2 receptor:anion ratio, and K_2 is greater than K_1, implying that binding of the first anion has a positive allosteric effect, favouring binding of the second anion.

Another example of using the transition metal to enhance electrostatic attraction rather than in a sensing role is shown in Fig. 45 [94]. Crystal structures of **127** with *p*-nitrophenolate, *p*-aminobenzoate and (L)-phenylalaninate show that the anions bind in the cavity by hydrogen bonding to the receptor oxygen and nitrogen atoms. Proton NMR titrations in DMSO-d_6 show log K values of 4.2–4.5 M^{-1} for **127** with the aromatic anionic guests, and a log K of only 3.3 M^{-1} with acetate, suggesting that π-stacking may enhance binding strength.

5. Conclusions

This review has described a variety of transition metal and organometallic based systems, which are capable of



126 **127**

Fig. 45. Receptors utilising electrostatic attractions.

recognising and sensing anionic guest species in both organic and aqueous media. The metallocenes cobaltocenium and ferrocene have proven particularly useful in the development of electrochemical anion sensors, in which the binding process may be detected by a cathodic shift in the metallocene redox potential. Ruthenium(II) and rhenium(I) bipyridyl based receptors represent a considerable contribution to the area of optical anion sensors, in which anion binding may be detected by changes in the molecules' luminescence properties. The presence of hydrogen bonding groups such as amides in both classes of receptor greatly enhances the anion binding capability. In general, the observed anion thermodynamic stability and selectivity trends can be rationalised in terms of complementary receptor-anion guest size, binding site topology and anion basicity. There is a current drive to exploit new and varied transition metal and organometallic systems in the search for novel responsive anion receptors. Such strategies include ion-pair receptors, the metal-directed self-assembly of receptor systems, and also systems which utilise the coordinating properties of transition metals. As this field of endeavour expands, our understanding of the nature of anions is increasing, and receptor design is becoming considerably more sophisticated. Many of these receptors have potential commercial applications, and there is no doubt that anion receptor chemistry is very much in the ascendancy.

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