

Transition-Metal Receptor Systems for the Selective Recognition and Sensing of Anionic Guest Species

PAUL D. BEER

Inorganic Chemistry Laboratory, University of Oxford, South Parks Road, Oxford OX1 3QR, U.K.

Received July 8, 1997

Introduction

Inspired by nature's fundamental biological processes involving enzyme–substrate or receptor–guest interactions, which are regulated via light, ions, or small molecule concentrations, and with the aim of advancing chemical sensor technology, considerable recent attention has focused on a new generation of abiotic host molecules that contain signaling or responsive functional groups as an integral part of a host macrocyclic framework.¹ The incorporation of a redox and/or optical signaling moiety in close proximity to a host binding site enables the host to be used as a prototype sensor for a target guest species as binding will perturb its electrochemical and/or photophysical properties (Figure 1). Although we^{1,2} and others³ have incorporated transition-metal and organic redox-active centers into a variety of crown ether, and cryptand, structural frameworks and shown some of these compounds to selectively electrochemically recognize cationic guest species, the development of responsive ligand systems for *anionic*⁴ guest species is only now being realized.⁵ This is surprising in view of the numerous indispensable roles anions play in biological and chemical processes⁶ and the importance of detecting/extracting anionic pollutants⁷ such as phosphate and nitrate, excess amounts of which lead to eutrophication and consequent disruption of aquatic life cycles. Radioactive pertechnetate⁸ anions also cause a pollution problem in the nuclear fuel cycle.

Since the birth of the field of anion coordination chemistry in the late 1960s,⁹ the main strategies in the design of synthetic anion complexing reagents have focused on cationic polyammonium,¹⁰ polyguanidinium,¹¹

Paul D. Beer obtained a first class honours degree in chemistry from King's College London in 1979. He remained there to undertake research in the field of organophosphorus chemistry under the supervision of Dr. C. D. Hall. In 1982, he received a Ph.D. and a Royal Society postdoctoral fellowship enabled him to conduct research in supramolecular chemistry with Professor J.-M. Lehn at the Université Louis Pasteur, Strasbourg, France. After a demonstratorship at the University of Exeter in 1983, in 1984, he took up a New Blood Lectureship at the University of Birmingham. In 1990, he moved to a lectureship at the Inorganic Chemistry Laboratory, University of Oxford, where he is also a tutorial fellow at Wadham College.

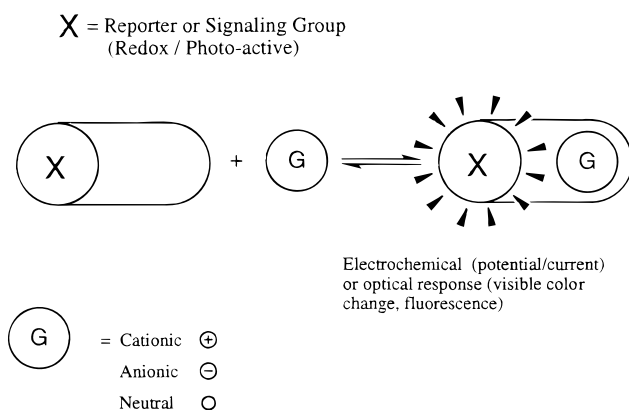


FIGURE 1. Depiction of the concept of electrochemical/optical recognition. The binding of guest species in close proximity to a redox and/or optical signaling moiety leads to an electrochemical and/or spectral response.

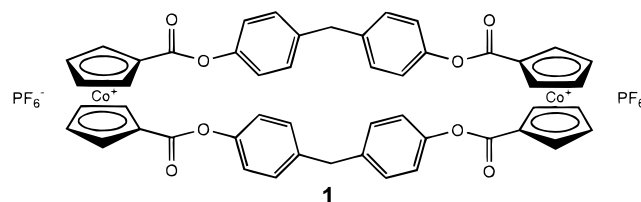


FIGURE 2. Bis-cobaltocenium macrocyclic receptor **1**.

quaternary ammonium,¹² expanded porphyrin¹³ host systems, and a variety of Lewis acidic containing receptors such as tin, silicon, boron, mercury,¹⁴ and uranyl.^{4e} Neutral organic receptors which bind anions solely via favorable hydrogen bonding interactions have also been recently exploited.¹⁵ We have initiated a research program aimed at the design and construction of innovative spectral and electrochemical sensory reagents for anions based on novel transition-metal organometallic and coordination receptor systems. Incorporating these inorganic signaling probes into various acyclic, macrocyclic, and calixarene ligand frameworks leads to new receptor systems capable of responding to anion recognition. This Account reviews our current progress in this field and highlights the major factors which dictate the anion selectivity trend and sensing proficiency a particular receptor exhibits.

Charged and Neutral Organometallic Metallocene Receptor Systems

Cobaltocenium-Based Receptors. The first redox-responsive class of anion receptor based on the redox-active positively charged cobaltocenium moiety was reported by us in 1989.¹⁶ The ester functionalized bis-cobaltocenium macrocyclic receptor **1** (Figure 2) bound and electrochemically sensed the bromide guest anion solely on favorable electrostatic interactions. Appending secondary amide functionalized “arms” to the cobaltocenium moiety introduced neutral hydrogen bond donor groups capable

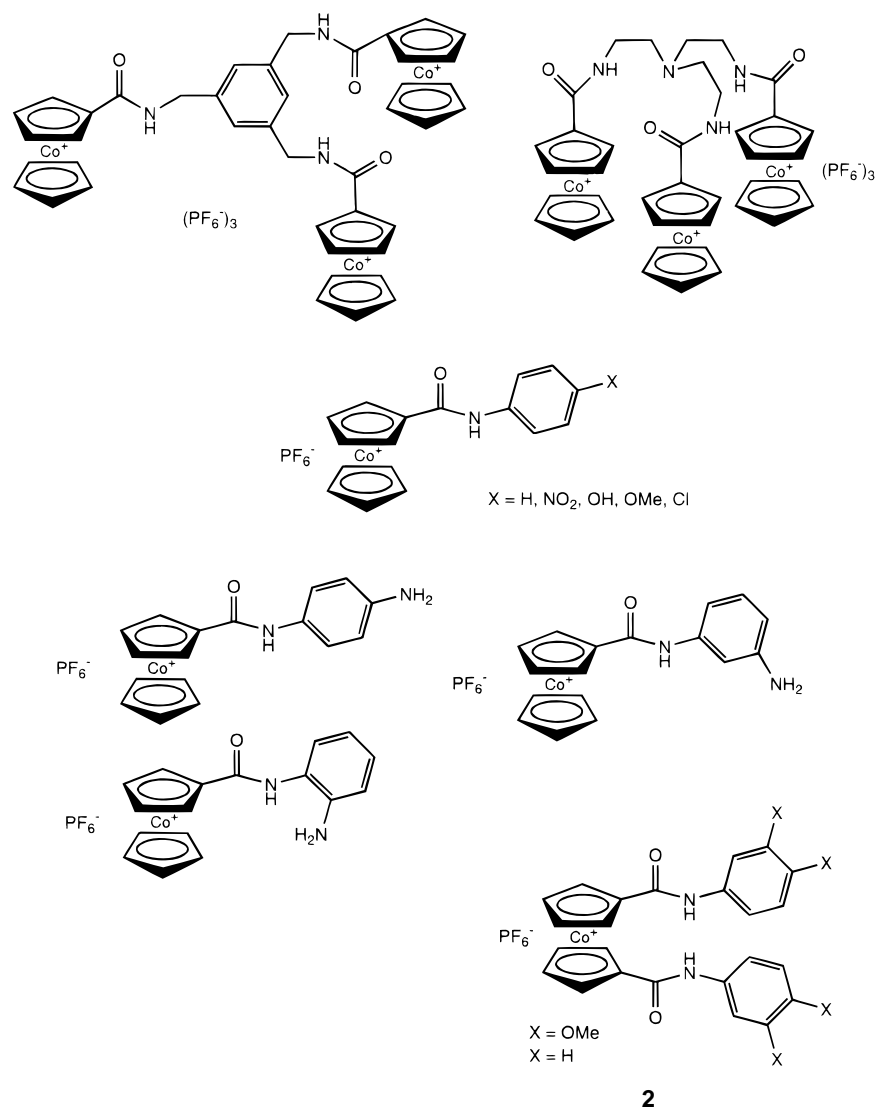


FIGURE 3. Acyclic, mono-, bis-, and tripodal amide-linked cobaltocenium receptors.

of coordinating anions. This synthetic strategy was used to prepare a variety of acyclic mono-, bis-, and tripodal amide-linked cobaltocenium receptors¹⁷ (Figure 3). On titration with tetrabutylammonium anion salts, proton NMR spectroscopy revealed large downfield shifts of receptor protons in polar aprotic solvents such as acetonitrile and dimethyl sulfoxide. Particularly perturbed was the amide proton, indicative of strong host amide -CO-NH- anion guest hydrogen bond formation. In the case of hosts where the amide was tertiary however, no anion binding was observed, thus highlighting the essential nature of the amide proton in the anion-binding process. This class of receptor therefore binds anions through a combination of hydrogen bonding with amide protons and electrostatic interaction with the positively charged cobaltocenium center. This is again featured in the crystal structure of receptor **2** with bound bromide anion, showing Br⁻ hydrogen bonding to the amide proton and also to C_p and aryl protons¹⁸ (Figure 4). Cyclic voltammetric experiments demonstrated that these cobaltocenium receptors had the capability of electrochemically recognizing anions; the redox potential of the reversibly reducible

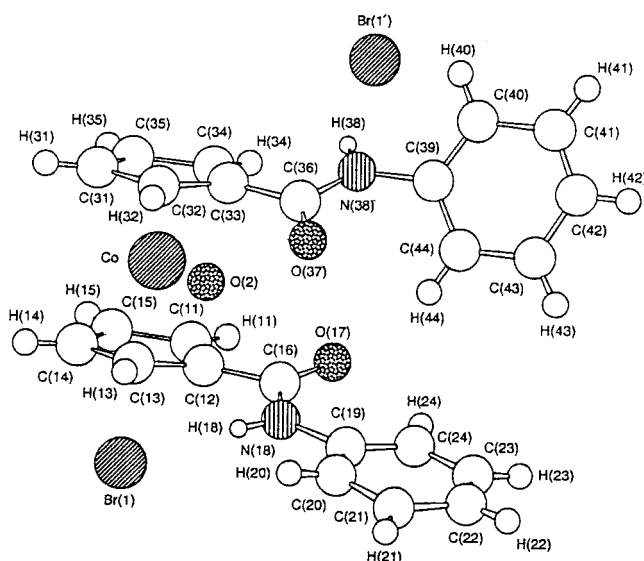


FIGURE 4. Structure of the bromide complex of **2**.

cobaltocenium moiety was significantly cathodically perturbed (Figure 5). The complexed anion effectively sta-

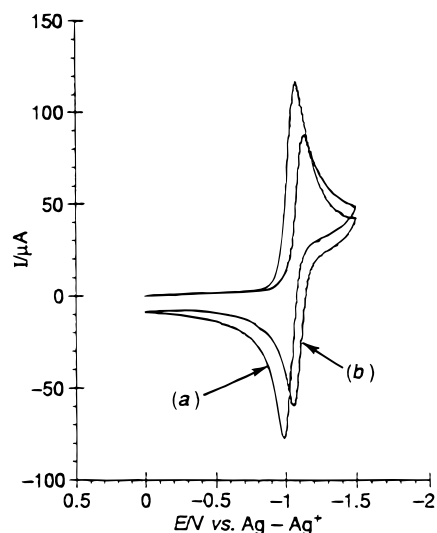


FIGURE 5. Cyclic voltammograms in acetonitrile of **2** in the absence (a) and presence (b) of excess chloride ion.

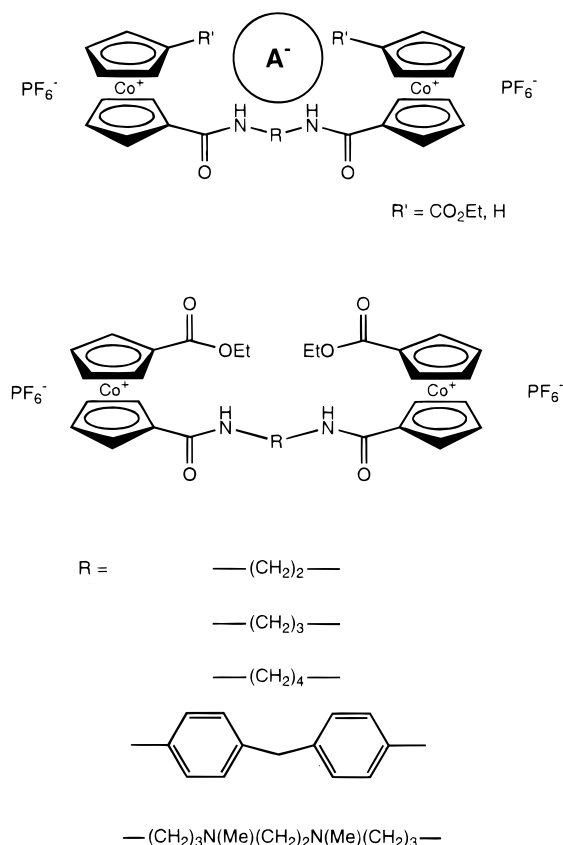


FIGURE 6. Ditopic bis-cobaltocenium receptors.

bilizes the positive charge, making the cobaltocenium unit more difficult to reduce. Large magnitudes of cathodic perturbations of up to $\Delta E = 240$ mV were observed with the H_2PO_4^- anion guest, which complemented the stability constant data in which the highest K values were obtained with this anion.¹⁸

In an attempt to further selectivity and enhance complex stability with this class of anion receptor, a series of ditopic bis-cobaltocenium systems with alkyl linkages were prepared and shown, from ¹H NMR titration studies, to form 1:1 complexes with halide anions¹⁹ (Figure 6).

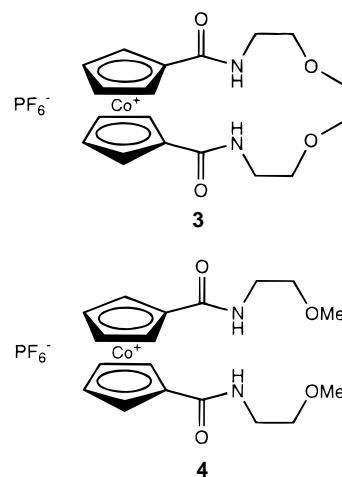


FIGURE 7. Macrocyclic amide-linked receptor **3** and acyclic receptor **4**.

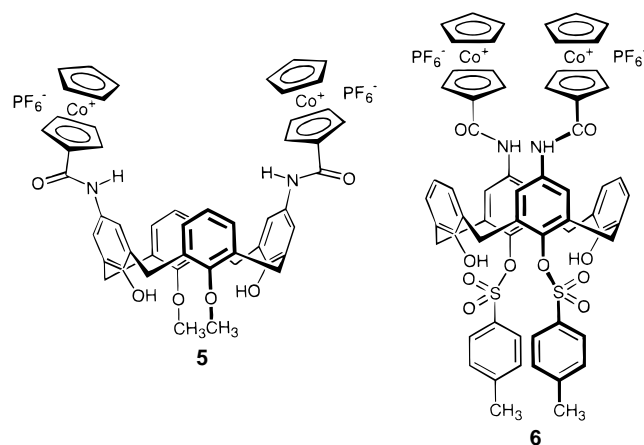


FIGURE 8. Bis-cobaltocenium calix[4]arene receptors **5** and **6**.

Stability constant evaluations indicated that, as the length of the alkyl chain increased, the general stability of the complex decreased, as did the degree of selectivity for chloride over bromide and iodide. The former observation provides experimental evidence for the existence of an anionic chelate effect. All the bis-cobaltocenium systems displayed electrochemical anion recognition with H_2PO_4^- , once again producing the largest magnitude of cathodic perturbation ($\Delta E = 250$ mV).

A macrocyclic receptor **3** has also recently been prepared²⁰ (Figure 7), and in comparison with its acyclic analogue **4**, an anion macrocyclic effect was observed, the stability constants for chloride complex formation in DMSO being $K = 250 \text{ M}^{-1}$ **3** and $K = 20 \text{ M}^{-1}$ **4**.

The unique topological calix[4]arene²¹ host structural framework has been recently modified for the recognition of anions.^{19,22} In particular, Atwood and co-workers, in a novel approach, have capped calixarene aromatic faces with positively charged transition-metal organometallic arene centers to produce a range of π -metalated calixarene anion receptors,^{4f,22c} one of which can recognize halide anions in aqueous media.^{22d} The bis-cobaltocenium calix[4]arene receptor¹⁹ **5** (Figure 8) was shown to form extremely stable 1:1 anion complexes in polar DMSO solutions as well as with the adipate anion in acetone. It

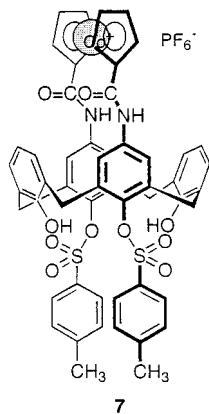


FIGURE 9. Upper-rim cobaltocenium-bridged calix[4]arene receptor 7.

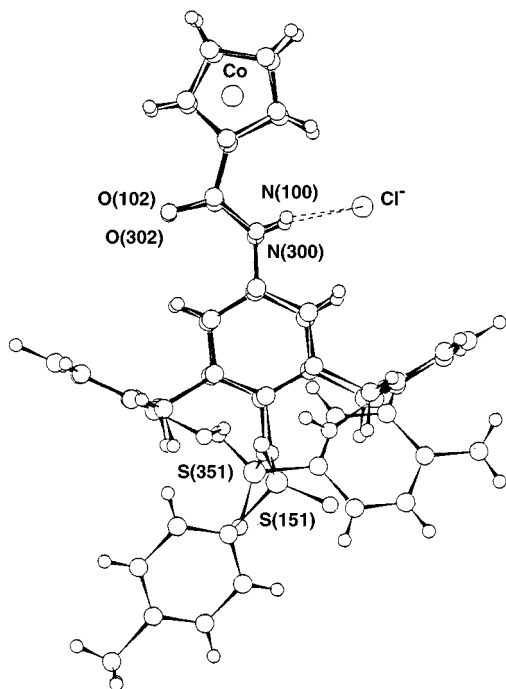
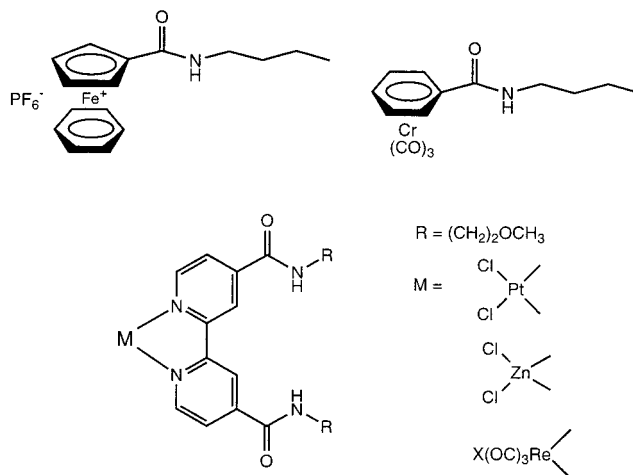


FIGURE 10. Structure of the chloride complex of 7.

is noteworthy that this receptor displayed an uncommon selectivity preference for chloride ($K = 5035 \text{ M}^{-1}$) over H_2PO_4^- ($K = 2800 \text{ M}^{-1}$). Modifying the functionality on the lower rim of this receptor, however, dramatically altered the anion selectivity properties.²³ For example, receptor **6** exhibits selectivity for H_2PO_4^- over Cl^- , the reverse of **5**. Presumably, the bulky tosyl groups alter the topology of the upper rim anion-binding site in favor of phosphate complexation. This result shows the capacity for facile-binding site manipulation in this class of receptor. This is further exemplified by the upper-rim cobaltocenium bridged calix[4]arene receptor **7**, which by virtue of its unique topology exhibits remarkable carboxylate anion selectivity²⁴ (Figure 9). For example, **7** complexes acetate with a stability constant of 41520 M^{-1} , which compares with $K = 70 \text{ M}^{-1}$ for chloride in DMSO solution. This has been attributed to the cobaltocenium bridging unit creating an ideal bidentate amide (CO-NH) hydrogen bond donor environment of complementary topology for



and 5,5'-bipy analogues

FIGURE 11. New classes of charged and neutral transition-metal organometallic and coordinated anion receptors.

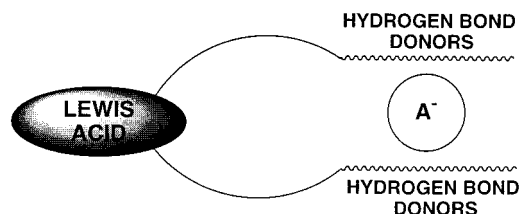


FIGURE 12. Schematic representation of the anion-binding protocol.

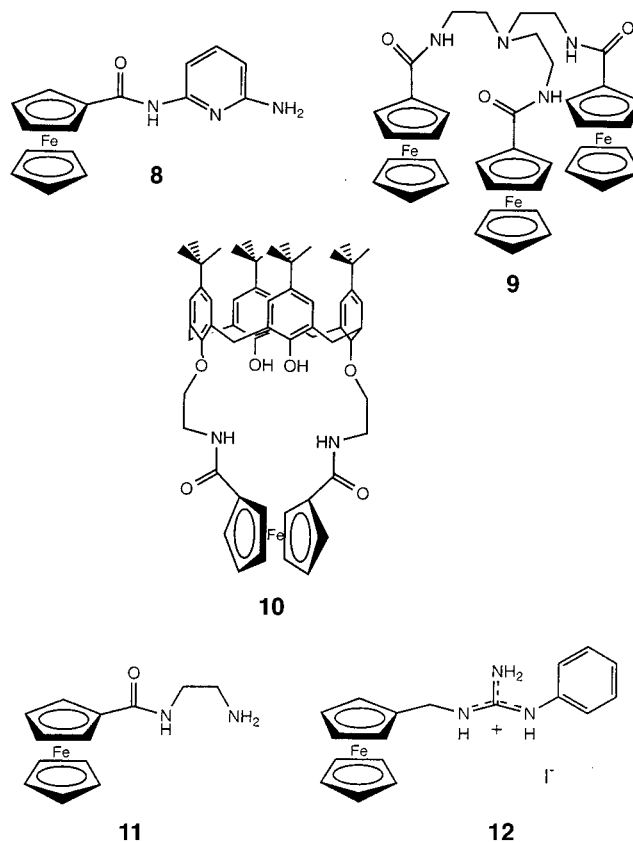


FIGURE 13. Ferrocene-based anion receptors recognizing the bidentate carboxylate anion. The X-ray crystal structure of the chloride complex of **7** corroborates this postulation (Figure 10). All of these receptors have

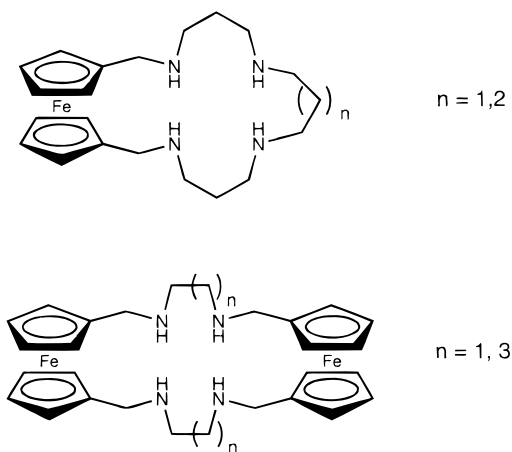


FIGURE 14. Polyaza ferrocene macrocycles.

been shown to electrochemically recognize the presence of anions through cathodic shifts in their cobaltocenium redox waves.

In an extension to the cobaltocenium anion receptor

protocol, experiments in our laboratory led to the syntheses of a series of new anion receptors which combined positively charged and neutral organometallic and coordinated transition-metal Lewis acidic units with secondary amide-binding sites²⁵ (Figure 11). Proton NMR anion titration experiments provided evidence for anion binding and established the generality of the principles of operation for this novel class of metal-based hydrogen-bonding anion receptors (Figure 12). This protocol for development of hydrogen-bond-based inorganic receptors has been of considerable general utility, as the following sections demonstrate.

Ferrocene-Based Receptors. Ferrocene units appended with secondary amides have been utilized for anion recognition²⁶ (Figure 13). Because of their neutrality, these receptors have no inherent electrostatic attraction with anions and consequently stability constants are much lower in magnitude than for the analogous positively charged cobaltocenium systems. Electrostatic interactions can, however, be switched on by oxidation of

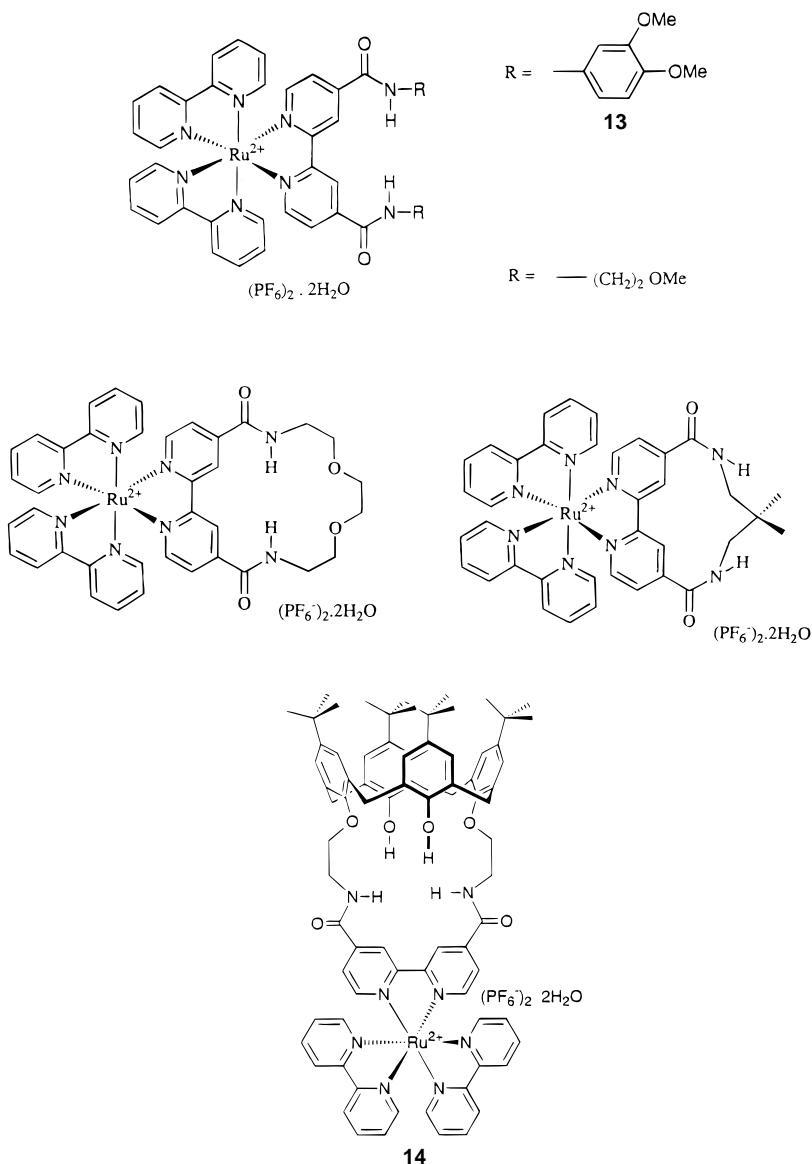


FIGURE 15. Acyclic, macrocyclic, and calix[4]arene ruthenium(II) bipyridyl receptors.

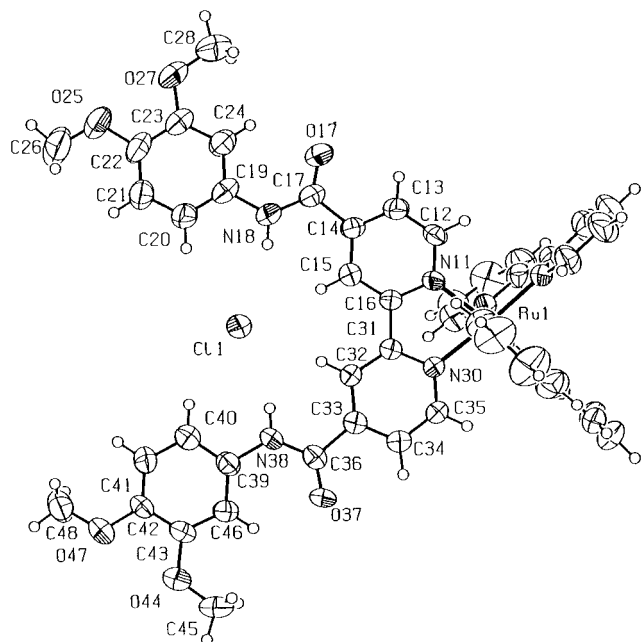


FIGURE 16. Structural view of the chloride complex of **13**.

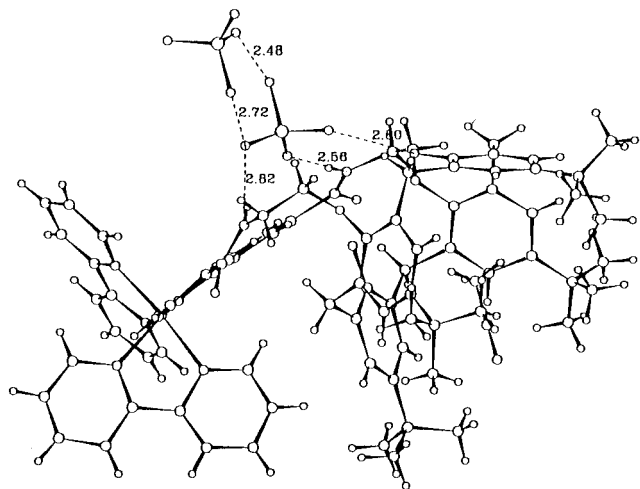
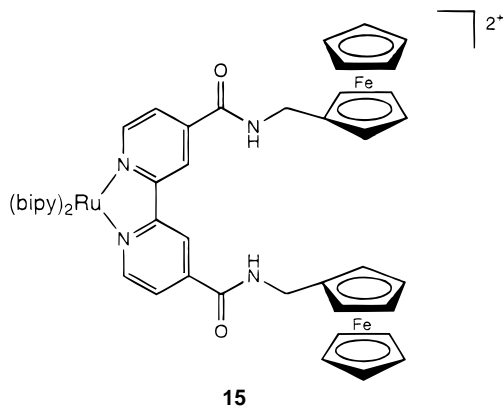


FIGURE 17. Structure of the dihydrogen phosphate complex of **14**. In the solid state, the anion hydrogen bonds to another anion molecule.

ferrocene to ferrocenium, and as a result, these receptors exhibit interesting electrochemical anion recognition effects and have a potential as amperometric anion sensors. Of interest to this development of sensor technology were the novel results of electrochemical competition experiments. These results demonstrated that **8–10** were capable of detecting H_2PO_4^- anions in the presence of 10-fold excess of HSO_4^- and Cl^- ions. Interestingly, in contrast, receptor **11** displays the reverse selectivity, binding HSO_4^- selectively in the presence of H_2PO_4^- . This novel anion selectivity is due to the presence of the basic amine functionality, which is protonated by the acidic hydrogen sulfate anion. This protonated receptor then shows a high binding affinity for the dinegative sulfate anions produced, which invoke a marked electrochemical reductive stripping response.

We have reported a series of water-soluble polyaza ferrocene macrocycles which are able to electrochemically



15

FIGURE 18. Ruthenium(II) bipyridyl-ferrocene receptor **15**.

recognize phosphate anions (HPO_4^{2-} , ATP) in an aqueous environment at pH 7 and below when they are partially protonated²⁷ (Figure 14). Ferrocene has also recently been combined with the guanidinium moiety to produce receptor **12**.²⁸ This molecule has been shown to electrochemically recognize the biologically important pyrophosphate anion in 50:50 water/methanol, with significant cathodic redox shifts of 70 mV. The ability of these receptors to function as sensors in biologically important media is of great importance.

Anion Complexation through Second-Sphere Coordination

Transition-Metal Bipyridyl Based Receptors. Another way of interpreting and hence exploiting the protocol for the development of hydrogen-bond-based inorganic anion receptors (Figure 12) is through using the second coordination sphere of metal complexes as a basis for anion recognition. Surprisingly, little attention has been paid to this approach and rare studies have mainly focused on the complexation of anions with cobalt amine complexes.²⁹

We recently incorporated the redox-active and photoactive ruthenium(II) bipyridyl moiety, in combination with secondary amide groups, into acyclic, macrocyclic, and lower-rim calix[4]arene structural frameworks to produce a new class of anion receptors capable of optical and electrochemical sensing³⁰ (Figure 15). Single-crystal X-ray structures of the chloride complex of **13** (Figure 16) and H_2PO_4^- complex of **14** (Figure 17) highlight again the importance of hydrogen bonding to the overall second-sphere anion complexation process. In the former complex (Figure 16), six hydrogen bonds (two amide and four C-H groups) stabilize the chloride, and in the latter, three hydrogen bonds (two amide and one calix[4]arene hydroxyl) effect H_2PO_4^- complexation (Figure 17). Stability constant determinations in DMSO demonstrated that the acyclic receptors form strong complexes with Cl^- and H_2PO_4^- anions, typically $K = 200\text{--}500\text{ M}^{-1}$ for Cl^- and 8000 M^{-1} for H_2PO_4^- . The ruthenium ion is dipositive, and hence, electrostatic interactions are particularly favorable. The macrocyclic receptors form highly selective and thermodynamically stable complexes with H_2PO_4^- .

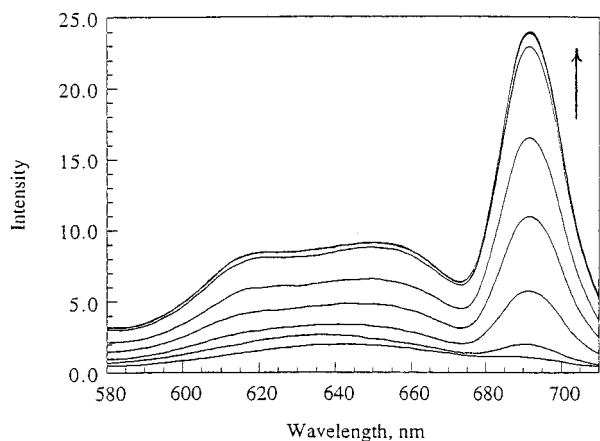


FIGURE 19. Effect of dihydrogen phosphate on the emission spectrum of **15**. Emission is induced most strongly at 690 nm by anion addition.

Electrochemical anion recognition experiments showed substantial anion-induced cathodic perturbation of the ligand-centered amide-substituted 2,2'-bipyridine reduction redox couple, with **14**, in agreement with stability constant values ($K = 28\,000\text{ M}^{-1}$ for H_2PO_4^-) in DMSO, capable of selectively sensing H_2PO_4^- in the presence of 10-fold excess amounts of HSO_4^- and Cl^- . Fluorescence emission measurements were also undertaken to probe the anion-binding process. All receptors exhibited significant blue shifts in the metal–ligand charge transfer (MLCT) λ_{max} emission band on addition of Cl^- and H_2PO_4^- , with **14** displaying the largest perturbation (16 nm). These shifts are *not* observed with unfunctionalized $[\text{Ru}(\text{bipy})_3]^{2+}$ and were accompanied by large increases in emission intensity (higher quantum yields). This may be a consequence of the bound anion rigidifying the receptor and inhibiting vibrational and rotational relaxation modes of nonradiative decay.

We also prepared an acyclic mixed-ruthenium(II) bipyferrocene receptor **15** (Figure 18), whose emission of the ruthenium center in the free receptor is quenched by the ferrocene units.³¹ However, on addition of dihydrogen phosphate anion, the emission increases 20-fold, being switched on by the presence of the anion (Figure 19). This effect was not observed with Cl^- or HSO_4^- ions. A competition experiment conducted in the presence of 5 equiv of both Cl^- and HSO_4^- reproduced the emission increase on addition of H_2PO_4^- , confirming the property of **15** as a H_2PO_4^- -selective luminescent anion sensor.

Novel dinuclear rhenium(I), ruthenium(II), and osmium(II) bipyridyl cleft-type receptor systems also exhibit remarkable selectivity for H_2PO_4^- over halide anions dependent upon the nature of the bridging linkage and the transition-metal Lewis-acidic center³² (Figure 20). Simply altering the linkage from *m*-phenylene to *p*-phenylene increased the magnitude of the stability constant of H_2PO_4^- by nearly a 100-fold from $K = 55\text{ M}^{-1}$ to $K = 4320\text{ M}^{-1}$ in DMSO, with the halide stability constant values remaining virtually unchanged. From electrostatic considerations, it was somewhat predictable that the neutral bis-rhenium(I) receptors form relatively weaker

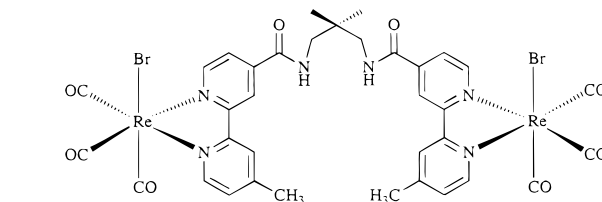
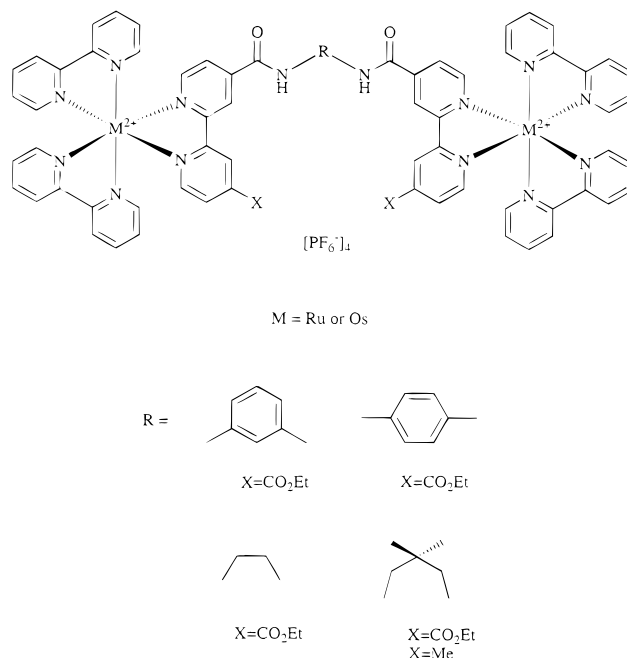


FIGURE 20. Dinuclear rhenium(I), ruthenium(II), and osmium(II) bipyridyl cleft-type receptors.

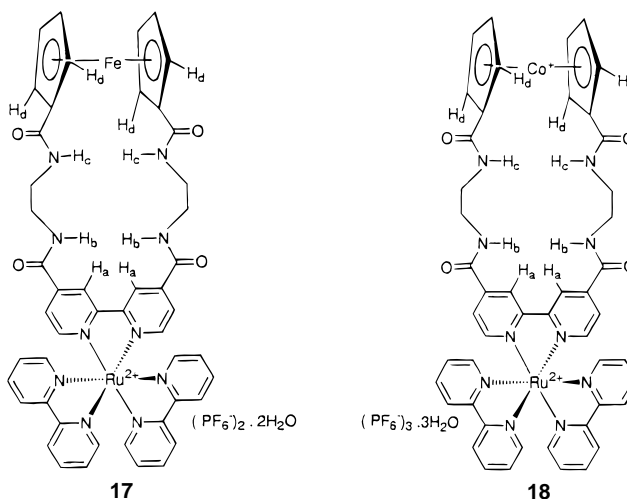
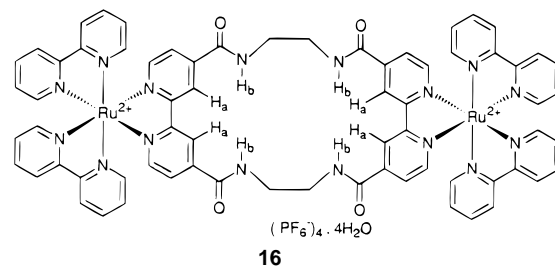


FIGURE 21. Macrocyclic bis(ruthenium(II) bipyridyl) **16** and ruthenium(II) bipyridyl–metallocene receptors **17** and **18**.

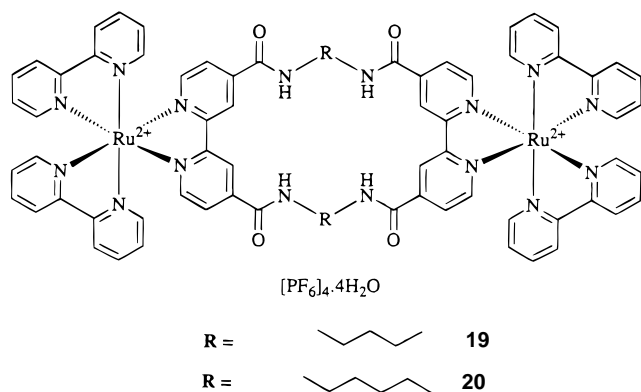


FIGURE 22. Larger ring sized bis(ruthenium(II) bipyridyl) macrocyclic receptors.

anion complexes than the charged ruthenium(II) and osmium(II) analogues. However, what was unexpected was, in comparison with the ruthenium(II) receptors, the dramatic increase in the magnitude of the stability constants for the osmium-containing receptors by over twofold for Cl⁻ ($K = 825 \text{ M}^{-1}$) and H₂PO₄⁻ ($K = >30\,000 \text{ M}^{-1}$), suggesting that the (bpy)₂Os²⁺ moiety is a particularly efficient Lewis-acidic center.

It is noteworthy that few of the receptors discussed so far exhibit specific binding and sensing of the chloride anion, yet this substrate is crucial for a large number of biological processes. We have recently prepared the novel macrocyclic bis[ruthenium(II) bipyridyl] and ruthenium(II) bipyridyl–metallocene receptors **16–18**^{33,34} (Figure 21). The ¹H NMR titrations indicated that each receptor

formed an extremely stable 1:1 stoichiometric complex with chloride in DMSO-*d*₆ solutions. In fact, the magnitudes of the stability constants are among the largest known for any anion–abiotic amide receptor complex (for **16**, $K = 40\,000 \text{ M}^{-1}$), 2 orders of magnitude greater than observed for the acyclic analogue. The ¹H and ³¹P NMR experiments proved that there was no or extremely weak dihydrogen phosphate anion binding in DMSO solution. This unique and remarkable selectivity may be attributed to the inherently rigid structures of the macrocycles, as the acyclic analogue binds H₂PO₄⁻ more strongly than Cl⁻. MM2 molecular modeling calculations suggest that the minimized structure of **16** has all the amide and 3,3'-bipyridyl protons lying in a coplanar arrangement, creating a host cavity of dimensions similar to those of the chloride anion. The larger size and tetrahedral shape of the H₂PO₄⁻ make this anion noncomplementary for the receptor's cavity.

Fluorescence studies indicated a blue-shift response to chloride with significant intensity enhancement but no response to H₂PO₄⁻. Receptors **16–18** are therefore prototype chloride-selective sensory reagents. Interestingly, increasing the size of the macrocyclic cavity by two or four methylene units dramatically reverses the anion selectivity trend;³⁴ **19** and **20** (Figure 22) selectively complex H₂PO₄⁻ over Cl⁻.

Recently, we have prepared the smaller pyridyl-linked macrocyclic receptor **21**, which exhibits the noteworthy selectivity trend AcO⁻ ≫ Cl⁻ > H₂PO₄⁻.³⁴ The crystal structure of the chloride complex of **21** (Figure 23) shows

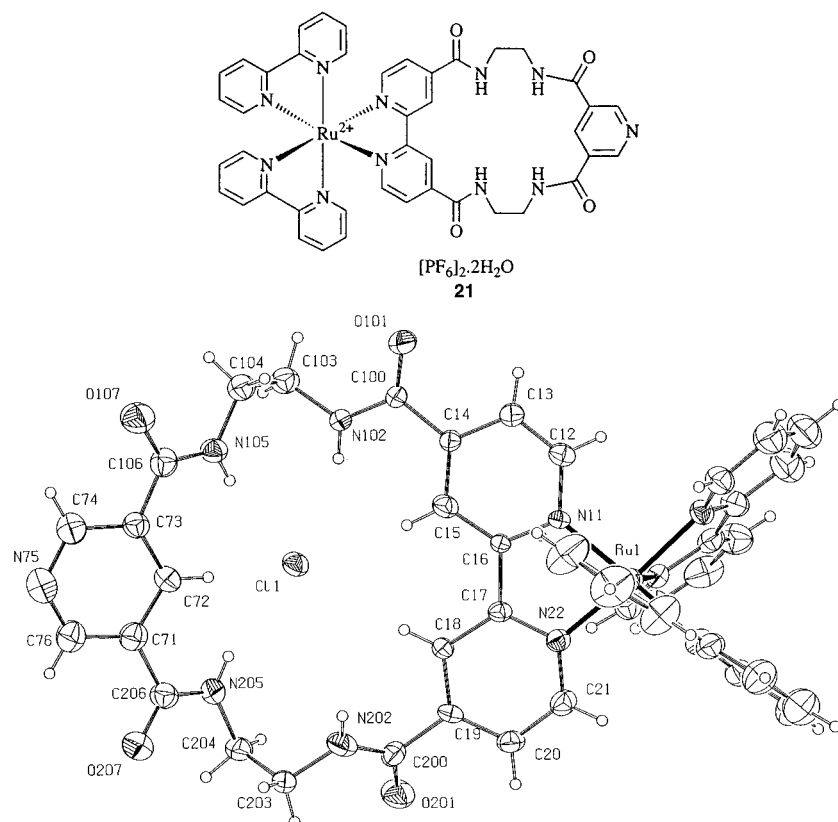


FIGURE 23. Structure of the chloride complex of **21**.

the halide anionic guest in the cavity stabilized by hydrogen bonding to amide, pyridyl, and bipyridyl protons.

Concluding Remarks

This Account has described a variety of transition-metal organometallic and coordination receptor systems capable of selectively recognizing and sensing anionic guest species by electrochemical and spectroscopic methods. We have seen that the incorporation of hydrogen bonding into these inorganic-based receptors is crucial to the anion recognition process. Their topological positioning in combination with the transition-metal Lewis-acidic centers prescribes anion complex thermodynamic stability and novel anion selectivity orders being observed. The optical/electrochemical sensing proficiency of each receptor is obviously dependent upon the nature of the redox-active/photoactive transition metal and the signaling unit's proximity to the anion-binding site. With these basic concepts now realized, the anion coordination chemist is now in a position to fabricate these types of systems into membranes, electronically conducting polymeric supports, and optical fibers to produce first-generation prototype sensory devices of prospective commercial interest.³⁵

I thank my postgraduate and postdoctoral co-workers for all their efforts; their names appear in the references. A special thank you goes to Dr. Michael G. B. Drew for his numerous structure determinations and molecular modeling expertise. I gratefully acknowledge the financial support of EPSRC, The Royal Society, Kodak Limited, British Petroleum, Serpentix, and the Ministry of Defence.

References

- (1) (a) Beer, P. D. *Chem. Soc. Rev.* **1989**, *18*, 409. (b) Beer, P. D. *Adv. Inorg. Chem.* **1992**, *39*, 79.
- (2) (a) Beer, P. D.; Chen, Z.; Drew, M. G. B.; Kingston, J. E.; Ogden, M. I.; Spencer, P. *J. Chem. Soc., Chem. Commun.* **1993**, 1046. (b) Chen, Z.; Pilgrim, A. J.; Beer, P. D. *J. Chem. Soc., Faraday Trans.* **1995**, *91*, 4331.
- (3) (a) Medina, J. C.; Goodnow, T. T.; Rojas, M. T.; Atwood, J. L.; Lynn, B. C.; Kaifer, A. E.; Gokel, G. W. *J. Am. Chem. Soc.* **1992**, *114*, 10583. (b) Hall, C. D.; Tucker, J. H. R.; Sheridan, A.; Chu, S. Y. F.; Williams, D. J. *J. Chem. Soc., Dalton Trans.* **1992**, 3133. (c) Plenio, H.; Diodone, R. *Inorg. Chem.* **1995**, *35*, 3964. (d) Tendero, M. J. L.; Benito, A.; Martinez-Manez, R.; Soto, J.; Paya, J.; Edwards, A. J.; Raithby, P. R. *J. Chem. Soc., Dalton Trans.* **1996**, 343.
- (4) (a) Schmidtchen, F. P. *Nachr. Chem. Tech. Lab.* **1988**, *8*, 10. (b) Katz, H. E. In *Inclusion Compounds*; Atwood, J. L., Davies, J. E. D., MacNicol, D. D., Eds.; Academic Press: New York, 1991; Vol. 4, p 391. (c) Sessler, J. L.; Burrell, A. K. *Top. Curr. Chem.* **1992**, *161*, 177. (d) Dietrich, B. *Pure Appl. Chem.* **1993**, *65*, 1457. (e) Reinhoudt, D. N.; Rudkevich, D. M.; Stauthamer, W. R. P. V.; Verboom, W.; Engersen, J. F. J.; Harkenna, S. *J. Am. Chem. Soc.* **1994**, *116*, 4341. (f) Atwood, J. L.; Holman, K. T.; Steed, J. W. *Chem. Commun.* **1996**, 1401. (g) Beer, P. D.; Smith, D. K. *Prog. Inorg. Chem.* **1997**, *46*, 1. (h) Beer, P. D. *Chem. Commun.* **1996**, 689.
- (5) (a) Czarnik, A. W. *Acc. Chem. Res.* **1994**, *27*, 302. (b) de Silva, A. P.; Gunarative, H. Q. N.; McVeigh, C.; Maguire, G. E. M.; Maxwell, P. R. S.; O'Hanlon, E. O. *Chem. Commun.* **1996**, 2191. (c) Fabbrizzi, L.; Francese, G.; Licchelli, M.; Perrotti, A.; Taslietti, A. *Chem. Commun.* **1997**, 581.
- (6) Frausto da Silva, J. J. R.; Williams, R. J. P. *Struct. Bonding (Berlin)* **1976**, *29*, 67.
- (7) Mason, C. F. *Biology of Freshwater Pollution*, 2nd ed.; Longman: Harlow, U.K., 1991.
- (8) Holm, E. *Radiochim. Acta* **1993**, *63*, 57.
- (9) Park, C. H.; Simmons, H. E. *J. Am. Chem. Soc.* **1968**, *90*, 2431.
- (10) (a) Dietrich, B.; Hossein, M. W.; Lehn, J. M.; Sessions, R. B. *J. Am. Chem. Soc.* **1981**, *103*, 1282. (b) Kimura, E.; Kodama, M.; Yatsunami, T. *J. Am. Chem. Soc.* **1982**, *104*, 3182. (c) Dietrich, B.; Guilheim, J.; Lehn, J. M.; Pascard, C.; Sonveaux, E. *Helv. Chim. Acta* **1984**, *67*, 91.
- (11) (a) Dietrich, B.; Fyles, D. L.; Fyles, T. M.; Lehn, J. M. *Helv. Chim. Acta* **1979**, 2763. (b) Echavarren, A.; Galán, A.; de Mendoza, J.; Salmeron, A.; Lehn, J. M. *Helv. Chim. Acta* **1988**, *71*, 685.
- (12) (a) Schmidtchen, F. P. *Chem. Ber.* **1980**, *113*, 864. (b) Schmidtchen, F. P.; Muller, G. *J. Chem. Soc., Chem. Commun.* **1984**, 1115.
- (13) (a) Sessler, J. L.; Mody, J. D.; Ford, D. A.; Lynch, V. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 452. (b) Sessler, J. L.; Burrell, A. K. *Top. Curr. Chem.* **1992**, *161*, 177.
- (14) (a) Newcomb, M.; Madonik, A. N.; Blanda, M. T.; Judice, J. K. *Organometallics* **1987**, *6*, 145. (b) Jung, M. E.; Xia, H. *Tetrahedron Lett.* **1988**, *29*, 297. (c) Yang, X.; Knobler, C. B.; Zheng, Z.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1994**, *116*, 7142. (d) Katz, H. E. *J. Org. Chem.* **1985**, *50*, 5027. (e) Wuest, J. D.; Beauchamp, A. L.; Oliver, M. J.; Zacharic, B. *J. Am. Chem. Soc.* **1986**, *108*, 73.
- (15) (a) Pascal, R. A.; Spergel, J.; Engen, D. Van. *Tetrahedron Lett.* **1986**, *27*, 4099. (b) Reinhoudt, D. N.; Valiyaveetil, S.; Engbersen, J. F. J.; Verboom, W. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 900. (c) Nishizawa, S.; Buhlmann, P.; Iwao, M.; Umezawa, Y. *Tetrahedron Lett.* **1995**, *36*, 6483.
- (16) Beer, P. D.; Keefe, A. D. *J. Organomet. Chem.* **1989**, *375*, C40.
- (17) (a) Beer, P. D.; Heseck, D.; Hodacova, J.; Stokes, S. E. *J. Chem. Soc., Chem. Commun.* **1992**, 270. (b) Beer, P. D.; Hazlewood, C.; Heseck, D.; Hodacova, J.; Stokes, S. E. *J. Chem. Soc., Dalton Trans.* **1993**, 1327.
- (18) Beer, P. D.; Drew, M. G. B.; Graydon, A. R.; Smith, D. K.; Stokes, S. E. *J. Chem. Soc., Dalton Trans.* **1995**, 403.
- (19) Beer, P. D.; Heseck, D.; Kingston, J. E.; Smith, D. K.; Stokes, S. E.; Drew, M. G. B. *Organometallics* **1995**, *3288*.
- (20) Beer, P. D.; Drew, M. G. B.; Hodacova, J.; Stokes, S. E. *J. Chem. Soc., Dalton Trans.* **1995**, 3447.
- (21) (a) Gutsche, C. D. *Calixarenes*; Stoddart, J. F., Ed. Monographs in Supramolecular Chemistry; The Royal Society of Chemistry: Cambridge and London, 1989; Vol 1. (b) Böhmer, V. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 713.
- (22) (a) Morzherin, Y.; Rudkevich, D. M.; Verboom, W.; Reinhoudt, D. N. *J. Org. Chem.* **1993**, *58*, 7602. (b) Rudkevich, D. M.; Verboom, W.; Reinhoudt, D. N. *J. Org. Chem.* **1994**, *59*, 3683. (c) Steed, J. W.; Junega,

- R. K.; Atwood, J. L. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2456. (d) Staffilani, M.; Hancock, K. S. B.; Steed, J. W.; Holman, K. T.; Atwood, J. L.; Junega, R. K.; Burkhalter, R. S. *J. Am. Chem. Soc.* **1997**, *119*, 6324.
- (23) Beer, P. D.; Drew, M. G. B.; Heseck, D.; Shade, M.; Szemes, F. *Chem. Commun.* **1996**, 2161.
- (24) Beer, P. D.; Drew, M. G. B.; Heseck, D.; Nam, K. C. *Chem. Commun.* **1997**, 107.
- (25) Beer, P. D.; Chen, Z.; Goulden, A. J.; Graydon, A. R.; Stokes, S. E.; Wear, T. *J. Chem. Soc., Chem. Commun.* **1993**, 828.
- (26) (a) Beer, P. D.; Chen, Z.; Goulden, A. J.; Graydon, A. R.; Stokes, S. E. *J. Chem. Soc., Chem. Commun.* **1993**, 1834. (b) Beer, P. D.; Graydon, A. R.; Johnson, A. O. M.; Smith, D. K. *Inorg. Chem.* **1997**, *36*, 2112. (c) Chen, Z.; Graydon, A. R.; Beer, P. D. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 97.
- (27) (a) Beer, P. D.; Chen, Z.; Drew, M. G. B.; Kingston, J.; Ogden, M. I.; Spencer, P. *J. Chem. Soc., Chem. Commun.* **1993**, 1045. (b) Beer, P. D.; Chen, Z.; Drew, M. G. B.; Johnson, A. O. M.; Smith, D. K.; Spencer, P. *Inorg. Chim. Acta* **1996**, *246*, 143.
- (28) Beer, P. D.; Drew, M. G. B.; Smith, D. K. *J. Organomet. Chem.* **1997**, *543*, 259.
- (29) (a) Beck, M. T. *Coord. Chem. Rev.* **1968**, *3*, 91. (b) Taura, T. *J. Am. Chem. Soc.* **1979**, *101*, 4221.
- (30) Szemes, F.; Heseck, D.; Chen, Z.; Dent, S. W.; Drew, M. G. B.; Goulden, A. J.; Graydon, A. R.; Grieve, A.; Mortimer, R. J.; Wear, T.; Weightman, J. S.; Beer, P. D. *Inorg. Chem.* **1996**, *35*, 5868.
- (31) Beer, P. D.; Graydon, A. R.; Sutton, L. R. *Polyhedron* **1996**, *15*, 2457.
- (32) Beer, P. D.; Dent, S. W.; Hobbs, G. S.; Wear, T. *Chem. Commun.* **1997**, 99.
- (33) Beer, P. D.; Szemes, F. *J. Chem. Soc., Chem. Commun.* **1995**, 2245.
- (34) Beer, P. D.; Szemes, F.; Balzani, V.; Salà, C. M.; Drew, M. G. B.; Dent, S. W.; Maestri, M. *J. Am. Chem. Soc.* **1997**, *119*, 11864.
- (35) (a) Hutchins, R. S.; Bachas, L. G. In *Biofunctional Membranes*; Butterfield, D. A., Ed.; Plenum: New York, 1996; p 35. (b) Kriz, D.; Ramstrom, O.; Svensson, A.; Mosbach, K. *Anal. Chem.* **1995**, *67*, 2142. (c) Xiao, K. P.; Bühlman, P.; Nishizawa, S.; Amemiya, S.; Umezawa, Y. *Anal. Chem.* **1997**, *69*, 1038.

AR9601555