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Alkali metal cation cooperative anion recognition by heteroditopic bis(calix[4]arene) rhenium(I) bipyridyl and ferrocene receptor molecules

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New heteroditopic bis(calix[4]arene) rhenium(I) bipyridyl (L^1, L^2) and ferrocene (L^4) receptor molecules have been prepared and shown to bind a variety of anions at the upper rim and alkali metal cations at the lower rim. Proton NMR anion titration studies reveal the strength and selectivity of anion binding was dependent upon the presence of the calix[4]arene moieties and nature of the bridging group with the preorganised receptors L^1 and L^2 forming strong complexes in deuterated DMSO solutions. With L^1, L^2 and L^4 co-bound lithium, sodium and potassium cations were found to significantly enhance the strength of iodide binding in acetonitrile solutions with the largest positive cooperative binding effect observed with L^2 and sodium cations. Cyclic voltammetric investigations revealed L^4 to electrochemically recognise carboxylate and halide anions. In the presence of lithium cations the electrochemical response of L^4 to bromide anions was significantly amplified.

The design of new heteroditopic ligands for the simultaneous complexation of cationic and anionic guest species is a new emerging and topical field of coordination chemistry.[1–10] These multisite ligands can be tailored to exhibit novel cooperative and allosteric behaviour whereby the binding of one charged guest can influence, through electrostatic and conformational effects, the subsequent coordination of the pairing ion. Such systems have potential as new selective extraction and transportation reagents for metal salt ion pair species of environmental importance.[9] Rare examples of receptors containing covalent linked binding sites for anions and cations include Lewis-acidic boron,[1] uranyl[2] or polyammonium[3] centres combined with crown ether moieties and crown ether or urea functionalised calix[4]arene ionophores[4,5] which are capable of solubilising and transporting alkali metal salts across lipophilic membranes.[10] We have shown that charged or neutral transition metal organometallic and coordination amide containing receptor systems can selectively bind and sense anions.[11] In particular, benzo-15-crown-5 functionalised ruthenium(II) and rhenium(I) bipyridyl amide ditopic receptors exhibit anion selectivity properties remarkably dependent upon the presence of crown ether co-bound potassium cations.[6] Combining the known lower rim ester functionalised calix[4]arene alkali metal cation coordinating moiety[12] with transition metal amide anion recognition groups will create new heteroditopic calix[4]arene based receptors capable of the simultaneous binding of anions and cations. We report here, the syntheses and anion/cation coordination chemistry of new heteroditopic bis(calix[4]arene) rhenium(I) bipyridyl and ferrocene receptors which display cooperative upper rim binding of halide anionic guest species *via* lower rim complexation of alkali metal cations.[13]

Experimental

Instrumentation

Nuclear magnetic resonance spectra were obtained on a Bruker AM300 instrument using the solvent deuterium signal as internal reference, fast atom bombardment (FAB) mass spectra at the EPSRC mass spectrometry service, University of Wales, Swansea. Electrochemical measurements were carried out using an E. G. and G. Princeton Applied Research 362 scanning potentiostat, a glassy carbon working electrode, and a $Ag–Ag^+$ reference electrode was used throughout. Elemental analyses were performed at the Inorganic Chemistry Laboratory, University of Oxford.

Solvent and reagent pretreatment

Where necessary, solvents were purified prior to use and stored under nitrogen. Acetonitrile was predried over class 4A molecular sieves (4–8 mesh) and then distilled from calcium hydride. Unless stated otherwise, commercial grade chemicals were used without further purification. 25,26,27,28-Tetrahydroxycalix[4]arene **1**,[14] 4,4′-bis(chlorocarbonyl)-2,2′-bipyridine **9**[15] and 1,1′-bis(chlorocarbonyl)ferrocene **12**[16] were prepared according to literature procedures.

Syntheses

25,26,27-Trihydroxy-25-phenylmethoxycalix[4]arene 2. 25,26,27,28-Tetrahydroxycalix[4]arene **1** (10 g, 23.58 mmol) and K_2CO_3 (1.64 g, 11.88 mmol, 0.5 equiv.) were stirred in MeCN (50 ml) for 30 min. Benzyl bromide (2.83 ml, 23.58 mmol, 1.0 equiv.) was added to the mixture which was then refluxed overnight. The solvent was removed under reduced pressure and the residue stirred with water (30 ml) and CH_2Cl_2 (30 ml) for 10 min. The phases were separated and the aqueous phase extracted twice with CH_2Cl_2 (20 ml), the organic layers were combined and the solvent removed under reduced pressure. The residue was stirred with diethyl ether (50 ml) for 1 h and the resulting solid filtered off under suction and air dried to give the product as a fine white powder (9.28 g, 77% yield). ^{1}H NMR (300 MHz, CD_3CN) δ 3.49 (d (J = 13.5 Hz), 2H, CCH_2C), 3.55 (d (J = 13 Hz), 2H, CCH_2C), 4.12 (d (J = 13.5 Hz), 2H, CCH_2C), 4.37 (d (J = 13 Hz), 2H, CCH_2C), 6.68–7.24 (m 12H,

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ArH), 7.59–7.83 (m, 5H, ArH), 9.04 (br s, 3H, OH). Microanalysis: $C_{35}H_{30}O_4$ requires C, 81.69; H, 5.88. Found: C, 80.83; H, 5.90%. FAB-MS: *m*/*z* 515 $[MH]^+$, 537 $[M + Na]^+$.

25,26,27-Tris[(ethoxycarbonyl)methoxy]-28-phenylmethoxycalix[4]arene 3. Compound **2** (5.0 g, 9.73 mmol) and a large excess of K_2CO_3 (3.0 g, 21.7 mmol) were stirred for 30 min in MeCN (50 ml). An excess of ethyl bromoacetate (5.39 ml, 49 mmol) was added and the mixture was refluxed overnight under N_2. More ethyl bromacetate (1 ml, 9.02 mmol) was added and refluxing was continued for a further 24 h. The solvent was removed under reduced pressure and the residue stirred with water (30 ml) and CH_2Cl_2 (30 ml) for 20 min. The phases were separated and the aqueous layer extracted twice with CH_2Cl_2 (20 ml), the organic phases were recombined and the solvent removed under reduced pressure. The residue was stirred in diethyl ether (50 ml) for 1 h and the resulting precipitate of incompletely reacted material was filtered off and washed with diethyl ether (30 ml). The washings and filtrate were combined and the solvent removed under reduced pressure. The residue was stirred in ethanol for several hours and the resulting solid filtered off and air dried to give the product as a fine white powder (4.53 g, 60% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.23–1.32 (m, 9H, OCH_2CH_3), 3.07 (d, (J = 13.5 Hz), 2H CCH_2C, 3.25 (d (J = 13.5 Hz), 2H, CCH_2C), 4.16 (q (J = 7 Hz), 4H, OCH_2CH_3), 4.24 (q (J = 7 Hz), 2H, OCH_2CH_3), 4.42 (d (J = 13.5 Hz), 2H, CCH_2C), 4.59 (s, 4H, $COCH_2O$), 4.65 (s, 2H, $COCH_2O$), 4.65 (d (J = 13.5 Hz), 2H, CCH_2C), 5.01 (s, 2H, OCH_2Ph), 6.59–6.68 (m, 12H, ArH), 7.3–7.4 (m, 5H, ArH). Microanalysis: $C_{47}H_{48}O_{10}$ requires C, 73.06; H, 6.22. Found: C, 73.32; H, 5.78%. FAB-MS: *m*/*z* 773 $[MH]^+$, 795 $[M + Na]^+$.

25,26,27-Tri[(ethoxycarbonyl)methoxy]-28-hydroxycalix[4]arene 4. To a suspension of **3** (3.68 g, 4.76 mmol) stirring in EtOH (50 ml) was added an excess of 10% Pd on carbon (0.20 g) and an excess of anhydrous ammonium formate (1.0 g, 15.9 mmol) and the mixture was refluxed for 3 h. After cooling, CH_2Cl_2 (40 ml) was added to the mixture which was then filtered through a Celite® pad. The Celite® was washed with CH_2Cl_2 (2 × 50 ml) and the washings combined with the filtrate. The solvent was removed under reduced pressure. The residue was dissolved in a minimum amount of CH_2Cl_2 and stirred with EtOH. The resulting solid was filtered off and air dried to give the product as a white powder (2.06 g, 64% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.26 (t (J = 7 Hz), 3H, OCH_2CH_3), 1.33 (t (J = 7 Hz), 6H, OCH_2CH_3), 3.31 (d (J = 13.5 Hz), CCH_2C), 3.33 (d (J = 13.5 Hz), 2H, CCH_2C), 4.14 (q (J = 7 Hz), 2H, OCH_2CH_3), 4.28 (q (J = 7 Hz), 4H, OCH_2CH_3), 4.37 (d (J = 13.5 Hz), 2H, CCH_2C), 4.51 (d (J = 15.5 Hz), 2H, $COCH_2O$), 4.68 (d (J = 15.5 Hz), 2H, $COCH_2O$), 4.96 (d (J = 13.5 Hz), 2H, CCH_2C), 5.11 (s, 2H, $COCH_2O$), 6.19 (s, 1H, O*H*), 6.48–6.54 (m, 6H, ArH), 6.71 (t (J = 7.5 Hz), 1 Hz, *p*-ArH), 6.92 (t (J = 7.5 Hz), 1H, *p*-ArH), 7.05 (d (J = 7.5 Hz), 2H, *m*-ArH), 7.11 (d (J = 7.5 Hz), 2H, *m*-ArH). Microanalysis: $C_{40}H_{42}O_{10}$ requires C, 70.38; H, 6.16. Found: C, 70.20; H, 6.19%.

25,26,27-Tri[(ethoxycarbonyl)methoxy]-28-hydroxy-17-nitrocalix[4]arene 5. Ammonium nitrate (2.0 g, 25 mmol) was dissolved in a mixture of H_2O (10 ml) and conc. HCl (35%, 6 ml). This was then added to (4) (1.00 g, 1.38 mmol) dissolved in CH_2Cl_2 (20 ml). Two drops of acetic anhydride were added and the mixture stirred for 10 min. The phases were separated, and the solvent removed from the organic phase under reduced pressure. The residue was dissolved in a minimum of CH_2Cl_2, EtOH was added until a precipitate was formed and the solution stirred for 30 min. The precipitate was filtered off to give the product as a fine yellow crystalline powder (0.66 g, 62% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.28 (t (J = 7 Hz), 3H, OCH_2CH_3), 1.34 (t (J = 7 Hz), 6H, OCH_2CH_3), 3.33 (d (J = 13.5 Hz), 2H CCH_2C), 3.42 (d (J = 13.5 Hz), 2H, CCH_2C), 4.16 (q (J = 7 Hz), 2H, OCH_2CH_3), 4.30 (q (J = 7 Hz), 4H, OCH_2CH_3), 4.43 (d (J = 13.5 Hz), 2H, CCH_2C), 4.48 (d (J = 15.5 Hz), 2H, $COCH_2O$), 4.75 (d (J = 15.5 Hz), 2H, $COCH_2O$), 4.92 (d (13.5 Hz), 2H, CCH_2C), 5.03 (s, 2H, $COCH_2O$), 6.57–6.64 (m, 6H, ArH), 6.67 (t (J = 7.5 Hz), 1H, *p*-ArH), 7.04 (d (J = 7.5 Hz), 2H, *m*-ArH), 7.95 (s, 2H, *m*-ArH), 8.06 (s, 1H, OH). Microanalysis: $C_{40}H_{41}NO_{12}$ requires C, 66.02; H, 5.64; N, 1.93. Found: C, 65.87; H, 5.73; N, 1.84%. FAB-MS *m*/*z* 728 $[MH]^+$, 750 $[M + Na]^+$.

25,26,27,28-Tetra[(ethoxycarbonyl)methoxy]-17-nitrocalix[4]arene 6. Compound **5** (1.25 g, 1.71 mmol) and a large excess of K_2CO_3 (1.0 g, 7.24 mmol) were stirred for 30 min in dry MeCN (25 ml). An excess of ethyl bromoacetate (1 ml, 9 mmol) was added and the mixture was refluxed overnight under N_2. The solvent was removed under reduced pressure and the residue stirred with water (15 ml) and CH_2Cl_2 (15 ml) for 20 min. The phases were separated and the aqueous layer extracted twice with CH_2Cl_2 (10 ml). The organic phases were recombined and the solvent removed under reduced pressure. The residue was stirred in propan-2-ol (30 ml) for 3 h and the resulting solid filtered off under suction and air dried to give the product as a fine pale yellow powder (1.19 g, 85% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.25–1.33 (m, 12H, OCH_2CH_3) 3.26 (d (J = 14 Hz), 2H CCH_2C), 3.32 (d (J = 14 Hz), 2H, CCH_2C), 4.16-4.27 (m, 8H, OCH_2CH_3), 4.60 (s, 2H, $COCH_2O$), 4.65 (d (J = 16.5 Hz), 2H, $COCH_2O$), 4.77 (s, 2H, $COCH_2O$), 4.80 (d (J = 13 Hz), 2H, CCH_2C), 4.83 (d (J = 16.5 Hz), 2H, $COCH_2O$), 5.0 (d (J = 14 Hz), 2H, CCH_2C), 6.36 (s, 3H, ArH), 6.63 (t (J = 7.5 Hz), 2H, *p*-ArH), 6.68–6.93 (m, 4H, *m*-ArH), 7.23 (s, 2H, *m*-ArH). Microanalysis: $C_{44}H_{47}NO_{14}$ requires C, 64.94; H, 5.78; N, 1.72. Found: C, 64.66; H, 6.33; N, 1.64%. FAB-MS *m*/*z* 836 $[M + Na]^+$.

General procedure for synthesis of 17-amino-calix[4]arene derivatives 7 and 8

17-Amino-25,26,27,28-tetra[(ethoxycarbonyl)methoxy]calix[4]arene 7. A stirred suspension **6** (0.50 g, 0.62 mmol) and excess powdered Zn metal (0.25 g, 3.84 mmol) in EtOH (20 ml) was brought to reflux then conc. HC1 (35% 2 ml) was added with care and the mixture refluxed under N_2 for 2 h. The solution was filtered to remove the excess zinc, and the solvent removed under reduced pressure. The residue was stirred with H_2O (20 ml) and CH_2Cl_2 (20 ml) for 10 min, the phases separated, and the aqueous phase extracted twice with CH_2Cl_2 (20 ml). The organic phases were recombined and the solvent removed under reduced pressure to give the product as a white solid (0.46 g, 96% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.26–1.31 (m, 12H, OCH_2CH_3) 3.12 (d (J = 13.5 Hz), 2H, CCH_2C), 3.25 (d (J = 13.5 Hz), 2H, CCH_2C), 4.20 (q (J = 7 Hz), 8H, OCH_2CH_3), 4.64 (s, 2H, $COCH_2O$), 4.71 (s, 2H, $COCH_2O$), 4.73 (s, 2H, $COCH_2O$), 4.79 (d (J = 13.5 Hz), 2H, CCH_2C), 4.88 (d (J = 13.5 Hz), 2H, $COCH_2O$), 6.01 (s, 2H, *m*-ArH), 6.58–6.69 (m, 9H, ArH). Microanalysis: $C_{44}H_{49}NO_{12}\cdot H_2O$ requires C, 65.90; H, 6.41; N, 1.75. Found: C, 65.79; H, 6.47; N, 1.75%. FAB-MS *m*/*z* 807 $[M + Na]^+$.

17-amino-25,26,27-tri[(ethoxycarbonyl)methoxy]-28-hydroxycalix[4]arene 8. In an analogous procedure to the preparation of **7**, compound **5** (1.00 g, 1.38 mmol) was reacted to give the product as a white solid (0.83 g, 87% yield).

General procedure for the synthesis of bipy bis calixarenes 10 and 11

17-Bis-4,4′-(2,2′-bipyridine)carbamyl-25,26,27,28-tetra-[(ethoxycarbonyl)methoxy]calix[4]arene 10. 4,4′-Bis(chlorocarbonyl)-2,2′-bipyridine **9** (0.166 g, 0.59 mmol) was dissolved in CH_2Cl_2 (20 ml) and stirred with an excess of dry triethyl-

amine (2 ml) for 15 min under N_2. Compound **8** (0.97 g, 1.24 mmol) was added and the mixture stirred under N_2 overnight. Hydrochloric acid (1 M, 20 ml) was added and the mixture stirred for 20 min, the phases were separated and the organic phase washed with ammonia solution (1 M, 20 ml). The solvent was removed under reduced pressure and the residue dried *in vacuo*. The residue was dissolved in a minimum of CH_2Cl_2 and stirred with propan-2-ol (30 ml) for 1 h and the resulting solid filtered off to give the product as a yellow solid (0.86 g, 82% yield). ^{1}H NMR (300 MHz, DMSO-d_6) δ 1.21–1.26 (m, 24H, OCH_2CH_3), 3.22 (br d (J = 13 Hz), 8H, CCH_2C), 4.12–4.17 (m, 16H, OCH_2CH_3), 4.63–4.75 (m, 24H, CCH_2C, $COCH_2O$), 6.56–6.76 (m, 18H ArH), 7.25 (s, 4H, *o*-ArH), 7.91 (br s, 2H, bipy-H_5), 8.85 (s, 2H, bipy-H_3), 8.89 (br s, 2H, bipy-H_6), 10.38 (s, 2H, NH). Microanalysis: $C_{100}H_{102}O_{26}N_4 \cdot 5H_2O$ requires C, 64.37; H, 6.05; N, 3.00. Found: C, 64.40; H, 5.90; N, 2.93%. FAB-MS *m*/*z* 1775 $[M + H]^+$, 1797 $[M + Na]^+$, 911 $[M + 2Na]^{2+}$.

17-Bis-4,4′-(2,2′-bipyridine)carbamyl-25,26,27-tri[(ethoxycarbonyl)methoxy]-28-hydroxycalix[4]arene 11. In an analogous synthesis, 4,4′-bis(chlorocarbonyl)-2,2′-bipyridine **9** (0.17 g, 0.60 mmol) was reacted with **7** (0.83 g, 1.19 mmol) to give the product as a brown solid (0.81 g, 89% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.27 (t (J = 7.5 Hz), 6H, OCH_2CH_3), 1.34 (t (J = 7 Hz), 12H, OCH_2CH_3), 3.33 (d (J = 13.5 Hz), 4H C–CH_2C), 3.37 (d (J = 13.5 Hz), 4H, CCH_2C), 4.15 (q (J = 7.5 Hz), 4H, OCH_2CH_3), 4.29 (q (J = 7 Hz), 8H, OCH_2CH_3), 4.42 (d (J = 13.5 Hz), 4H, CCH_2C), 4.52 (d (J = 15.5 Hz), 4H, $COCH_2O$), 4.66 (d (J = 15.5 Hz), 4H, $COCH_2O$), 4.96 (d (J = 13.5 Hz), 4H, CCH_2C), 5.10 (s, 4H, $COCH_2O$), 6.55 (d (J = 7 Hz), 8H, *m*-ArH), 6.63 (t (J = 7 Hz), 4H, *p*-ArH), 6.93 (t (J = 7 Hz), 2H, *p*-ArH), 7.11 (d (J = 7 Hz), 4H, *m*-ArH), 7.43 (s, 4H, *m*-ArH), 7.94 (d (J = 5 Hz), 2H, bipy-H_5), 8.01 (s, 2H, NH), 8.64 (s, 2H, bipy-H_3), 8.90 (d (J = 5 Hz), 2H, bipy-H_6). Microanalysis: $C_{92}H_{90}N_4 \cdot H_2O$ requires C, 68.14; H, 5.72; N, 3.45. Found: C, 68.15; H, 5.60; N, 3.75%. FAB-MS *m*/*z* 1649 $[M + (2Na)]^{2+}$, 825 $[M + (2Na)]^{2+}$.

General synthesis of rhenium receptors L^1 and L^2

{17-Bis-4,4′-(2,2′-bipyridine)carbamyl-25,26,27,28-tetra-[(ethoxycarbonyl)methoxy] calix[4]arene} tricarbonylchlororhenium(I) L^2. Pentacarbonylchlororhenium(I) (0.0425 g, 0.12 mmol) was refluxed in 15 ml THF for 30 min. Compound **11** (0.19 g, 0.11 mmol) was then added and the mixture refluxed overnight. The solvent was removed under reduced pressure and the resulting solid purified by silica column chromatography, eluted with ethyl acetate and the first orange fraction collected. The solvent was removed under reduced pressure and the residue dissolved in a minimum of THF. Hexane was added to the mixture until an orange precipitate was formed, which was then filtered off and dried *in vacuo* to give the product as an orange solid (0.10 g, 45% yield). ^{1}H NMR (300 MHz, DMSO-d_6) δ 1.23 (t (J = 7 Hz), 24 H, OCH_2CH_3), 3.23 (d (J = 13 Hz), 8H, CCH_2C), 4.12–4.19 (m, 16H, OCH_2CH_3), 4.66–4.80 (m, 24H, CCH_2C, $COCH_2O$), 6.58–6.73 (m, 18H ArH), 7.22 (s, 4H, *o*-ArH), 8.11 (d (J = 5.5 Hz), 2H, bipy-H_5), 9.16 (s, 2H, bipy-H_3), 9.19 (d (J = 5.5 Hz), 2H, bipy-H_6), 10.54 (s, 2H, NH). Microanalysis: $C_{103}H_{102}N_4O_{29}ReCl \cdot 5H_2O$ requires C, 56.97; H, 5.16; N, 2.58. Found: C, 56.96; H, 5.03; N, 2.56%. FAB-MS *m*/*z* 2102 $[M + Na]^+$, 2160 $[M + (2Na + Cl)]^+$.

{17-Bis-4,4′-(2,2′-bipyridine)carbamyl-25,26,27-tri[(ethoxycarbonyl)methoxy]-28-hydroxycalix[4]arene}tricarbonylchlororhenium(I) L^1. In an analogous synthetic procedure pentacarbonylchlororhenium (0.062 g, 0.17 mmol) reacted with **10** (0.25 g, 0.15 mmol) to give the product as an orange solid (0.19 g, 64% yield) ^{1}H NMR (300 MHz, CD_3CN) δ 1.25 (t (J = 7 Hz), 6H, OCH_2CH_3), 1.32 (t (J = 7 Hz), 12H, OCH_2CH_3), 3.34 (d (J = 13 Hz), 8H CCH_2C), 4.14 (q (J = 7 Hz), 4H, OCH_2CH_3), 4.28 (q (J = 7 Hz), 8H, OCH_2CH_3), 4.34 (d (J = 13 Hz), 4H, CCH_2C), 4.44 (d (J = 16 Hz), 4H, $COCH_2O$), 4.64 (d (J = 16 Hz), 4H, $COCH_2O$), 4.85 (d (J = 13 Hz), 4H, C–CH_2C), 5.06 (s, 4H, $COCH_2O$), 6.59 (t (J = 7.5 Hz), 4H, *p*-ArH), 6.73 (d (J = 7.5 Hz), 8H, *m*-ArH), 6.89 (t (J = 7.5 Hz), 2H, *p*-ArH), 7.15 (d (J = 7.5 Hz), 4H, *m*-ArH), 7.51 (s, 4H, *o*-ArH), 8.01 (d (J = 5.5 Hz), 2H, bipy-H_5), 9.08 (s, 2H, bipy-H_3), 9.18 (d (J = 5.5 Hz), 2H, bipy-H_6), 9.24 (s, 2H, NH). Microanalysis: $C_{95}H_{90}N_4O_{25}ReCl \cdot H_2O$ requires C, 59.19; H, 4.78; N, 2.90. Found: C, 59.00; H, 4.78; N, 2.89%. FAB-MS *m*/*z* 1931 $[M + Na]^+$.

17-(Bisferrocene)carbamyl-25,26,27,28-tetra[(ethoxycarbonyl)methoxy]calix[4]arene L^4. 1,1–Bis(chlorocarbonyl)ferrocene **12** (0.0986 g, 0.32 mmol) was dissolved in CH_2Cl_2 (10 ml) and stirred with an excess of dry triethylamine (2 ml) for 40 min under N_2. Compound **8** (0.52 g, 0.64 mmol) in dry CH_2Cl_2 (10 ml) was added and the mixture stirred under N_2 overnight. HCl (1 M, 20 ml) was then added and the mixture was stirred for 20 min, the phases were separated and the solvent removed from the organic phases under reduced pressure and the residue dried *in vacuo*. The residue was dissolved in a minimum of CH_2Cl_2 and purified by silica column chromatography, eluted with 20% ethyl acetate in CH_2Cl_2 until a pale yellow band was collected and then the eluting mixture was changed to 1 : 1 ethyl acetate–CH_2Cl_2 and the first band collected. The solvent was removed under reduced pressure and the resulting solid dissolved in a minimum of CH_2Cl_2 from which the product was precipitated with pentane as a yellow solid (0.12 g, 21% yield). ^{1}H NMR (300 MHz, CD_3CN) δ 1.21–1.29 (m, 24H, OCH_2CH_3), 3.23 (d (J = 13.5 Hz), 4H, CCH_2C), 3.24 (d (J = 13.5 Hz), 4H, CCH_2C), 4.13–4.23 (m, 16H, OCH_2CH_3), 4.45–4.47 (m, 4H, Cp-H), 4.60 (s, 8H, $COCH_2O$), 4.68–4.70 (m, 4H, Cp-H), 4.77–4.84 (m, 16H, CCH_2C, $COCH_2O$), 6.50–6.83 (m, 18H ArH), 7.24 (s, 4H, *o*-ArH), 8.78 (s, 2H, NH). Microanalysis: $C_{100}H_{104}N_2O_{26}Fe \cdot 2H_2O$ requires C, 65.21; H, 5.81; N, 1.52. Found: C, 65.61; H, 7.00; N, 1.53%. FAB-MS *m*/*z* 1829 $[M + Na]^+$, 1887 $[M + (2Na + Cl)]^+$.

Bis-4-butoxyphenyl-4,4′-(2,2′-bipyridyl)carbamide. 4,4′-Bis-(chlorocarbonyl)-2,2′-bipyridine **9** (0.34, 1.67 mmol) was dissolved in CH_2Cl_2 (20 ml) and stirred with an excess of dry triethylamine (2 ml) for 15 min under N_2. 4-Butoxyaniline (0.61, 3.7 mmol, 2.2 equiv.) was added to the mixture with stirring. A precipitate formed immediately and the mixture was stirred for a further 3 h under N_2. The precipitate was filtered off and washed with successively MeCN (20 ml), NH_3(aq.) (20 ml), H_2O (40 ml), EtOH (40 ml), Et_2O (40 ml) and air dried to give the product as a pale pink solid (0.48 g, 53% yield). ^{1}H NMR insoluble in all deuterated solvents available. Microanalysis: $C_{32}H_{34}N_4O_4$ requires C, 71.36; H, 6.36; N, 10.40. Found: C, 70.95; H, 6.25; N, 10.29%.

Bis-4-butoxyphenyl-4,4′-(2,2′-bipyridine)carbamyltricarbonylchlororhenium(I) L^3. Pentacarbonyl chlororhenium(I) (0.14 g, 0.39 mmol) was refluxed in 15 ml THF for 30 min, bis-4-butoxyphenyl-4,4′(2,2′-bipyridine)carbamide (0.20 g, 0.37 mmol) was added and the mixture refluxed overnight. The resulting suspension was filtered to give the product as an orange solid (0.29 g, 95% yield). ^{1}H NMR (300 MHz, DMSO-d_6) δ 0.94 (t (J = 7.5 Hz), 6H, CH_2CH_3), 1.40–1.48 (m, 4H, CH_2), 1.67–1.72 (m, 4H, CH_2), 3.92 (t (J = 6.5 Hz), 4H, OCH_2CH_2), 6.98 (d (J = 9 Hz), 4H, ArH), 7.68 (d (J = 9 Hz), 4H, ArH), 8.16 (d (J = 6 Hz), 2H, bipy-H_5), 9.22 (s, 2H, bipy-H_3), 9.23 (d (J = 5.5 Hz), 2H, bipy-H_4), 10.76 (s, 2H, NH). Microanalysis: $C_{35}H_{34}N_4O_7ReCl$ requires C, 49.78; H, 4.02; N, 6.64. Found: C, 49.78; H, 4.10; N, 6.64%.

Table 1 Crystal data and structure refinement for **4**, **5** and **6**

	4	**5**	**6**
Empirical formula	$C_{40}H_{42}O_{10}$	$C_{42}H_{41}NO_{11}$	$C_{44}H_{47}NO_{14}$
M	682.74	723.75	813.83
Crystal system, space group	Monoclinic, $P2_1/c$	Monoclinic $P2_1/n$	Monoclinic $P2_1/n$
Unit cell dimensions			
a/Å	10.509(14)	13.193(15)	14.868(17)
b/Å	16.364(17)	21.08(2)	14.587(18)
c/Å	20.06(2)	14.730(16)	20.29(2)
β/°	94.73(1)	114.84(1)	110.32(1)
V/Å^3	3439	3717	4126
Z, D_c/Mg m^{-3}	4, 1319	4, 1.293	4, 1310
Reflections collected/unique (R_{int})	8977/5575 (0.0374)	19688/6060 (0.0264)	13134/7723 (0.0673)
Data/restraints/parameters	5575/0/456	6060/0/482	7723/0/537
Final R indices [$I > 2\sigma(I)$] $R1$	0.0828	0.0912	0.0843
$wR2$	0.2401	0.2714	0.2219
(all data) $R1$	0.1358	0.1386	0.2285
$wR2$	0.2841	0.3134	0.2906
Largest difference peak and hole/e Å^{-3}	0.574, −0.412	0.601, −0.402	0.218, −0.207

Crystallography

Crystal data (Table 1) were collected with Mo-Kα radiation using the MARresearch Image Plate System at room temperature. The crystals were positioned at 70 mm from the Image Plate. 100 frames were measured at 2° intervals with a counting time of 2 min. Data analysis was carried out with the XDS program.[17] The structures were solved using direct methods with the SHELX86 program.[18] The non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were included in geometric positions and given thermal parameters equivalent to 1.2 times those of the atom to which they were attached. The structures were refined on F^2 using SHELXL.[19]

CCDC reference number 186/2071.

See http://www.rsc.org/suppdata/dt/b0/b003569f/ for crystallographic files in .cif format.

^{1}H NMR titrations

A solution of the receptor (500 μl) was prepared at a concentration typically of the order of 0.01 mol dm^{-3} in deuterated dimethyl sulfoxide or acetonitrile. The initial ^{1}H NMR spectrum was recorded and aliquots of anion were added by gas-tight syringe from a solution made such that 1 mol equivalent was added in 20 μl. After each addition and mixing, the spectrum was recorded again and changes in the chemical shift of certain protons were noted. The result of the experiment was a plot of displacement in chemical shift as a function of the amount of added anion, which was subjected to analysis by curve-fitting since the shape is indicative of the stability constant for the complex. The computer program EQNMR[20] was used which requires the concentration of each component and the observed chemical shift (or its displacement) for each data point. Typically these titration experiments were repeated three times with at least fifteen data points in each experiment.

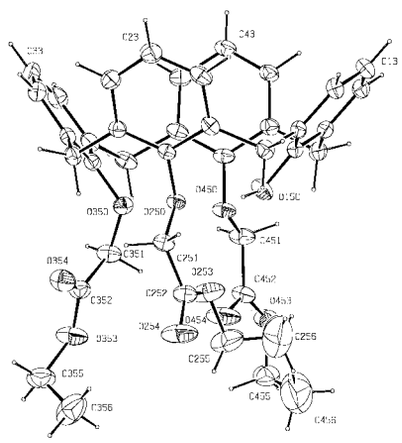


Fig. 1 The structure of **4** with ellipsoids at 20% probability.

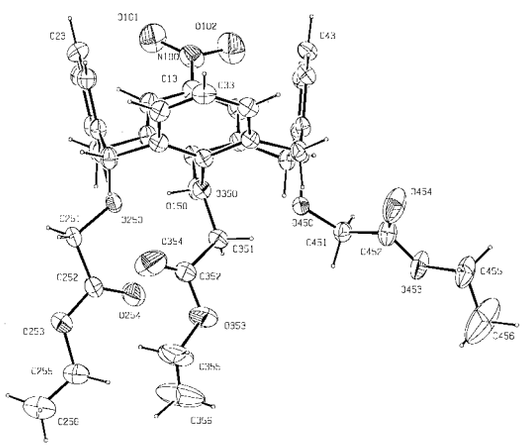


Fig. 2 The structure of **5** with ellipsoids at 20% probability.

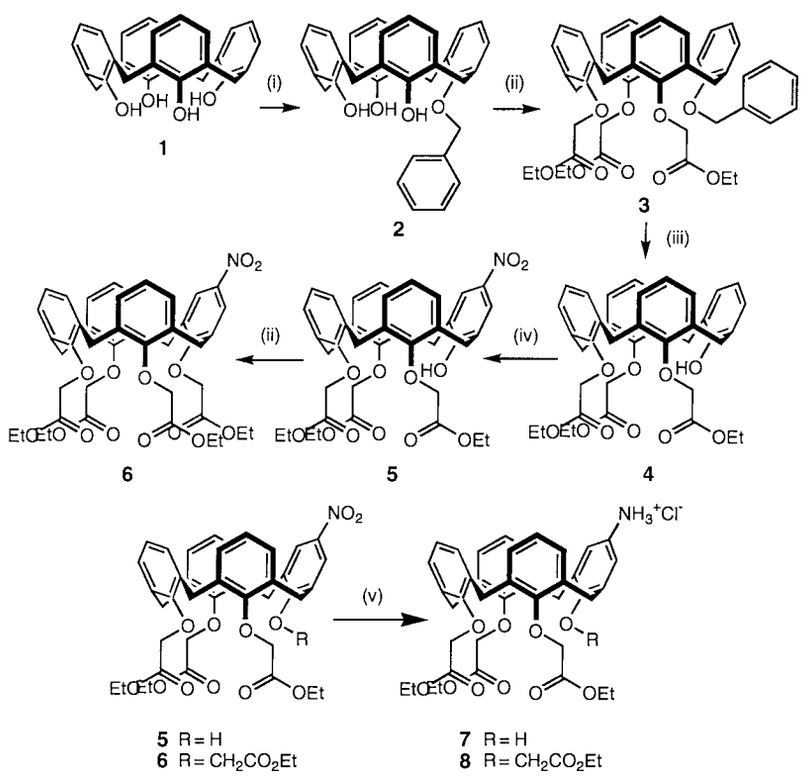
Results and discussion

Syntheses of mono-amine calix[4]arene synthons

The new upper rim mono-amine–lower rim ester substituted calix[4]arene derivatives **7** and **8** were prepared according to Scheme 1. The reaction of calix[4]arene **1**[14] with 1 equivalent of benzyl bromide in the presence of potassium carbonate gave the mono-substituted calix[4]arene **2** in 77% yield. Exhaustive alkylation of **2** with ethyl bromoacetate afforded the tetra-substituted product **3** in 60% yield. The benzyl protecting group was removed using ammonium formate and palladium/carbon catalyst to produce the triester **4** in a typical yield of 64%. Nitration of **4** to give **5** was achieved using ammonium nitrate, hydrochloric acid and a few drops of acetic anhydride. Treatment of **5** with an excess of ethyl bromoacetate gave the product **6** in 85% yield. Both nitro calixarenes were reduced to their corresponding amines **7** and **8** by treatment with zinc metal and concentrated hydrochloric acid and isolated as their hydrochloride salts (Scheme 1).

X-Ray structural investigations of compounds 4, 5 and 6

Crystals of **4**, **5** and **6** suitable for structural determination were grown from dilute ethanol solutions of the compounds. The three structures are shown in Figs. 1, 2 and 3, and all show the substituted calix[4]arene in the cone conformation, although with different distortions. The conformations can be quantified by the angles between the phenyl rings and the plane of the four



5 R = H
6 R = CH_2CO_2Et
7 R = H
8 R = CH_2CO_2Et

Scheme 1 *Reagents and conditions*: (i) 1 equiv. $PhCH_2Br$, 0.5 equiv. K_2CO_3, MeCN reflux, 24 h; (ii) $BrCH_2CO_2Et$ (excess), K_2CO_3 (excess), MeCN reflux, 48 h; (iii) Pd/C, HCO_2NH_4, EtOH reflux; (iv) NH_4NO_3, HCl, H_2O, acetic anhydride, CH_2Cl_2; (v) Zn (excess), HCl (excess), reflux EtOH, 24 h.

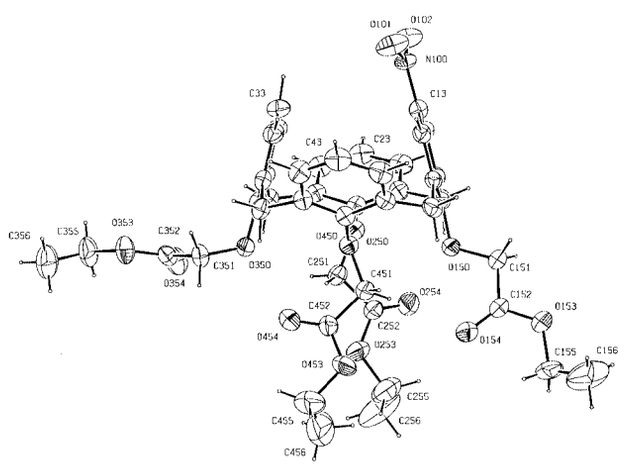


Fig. 3 The structure of **6** with ellipsoids at 20% probability.

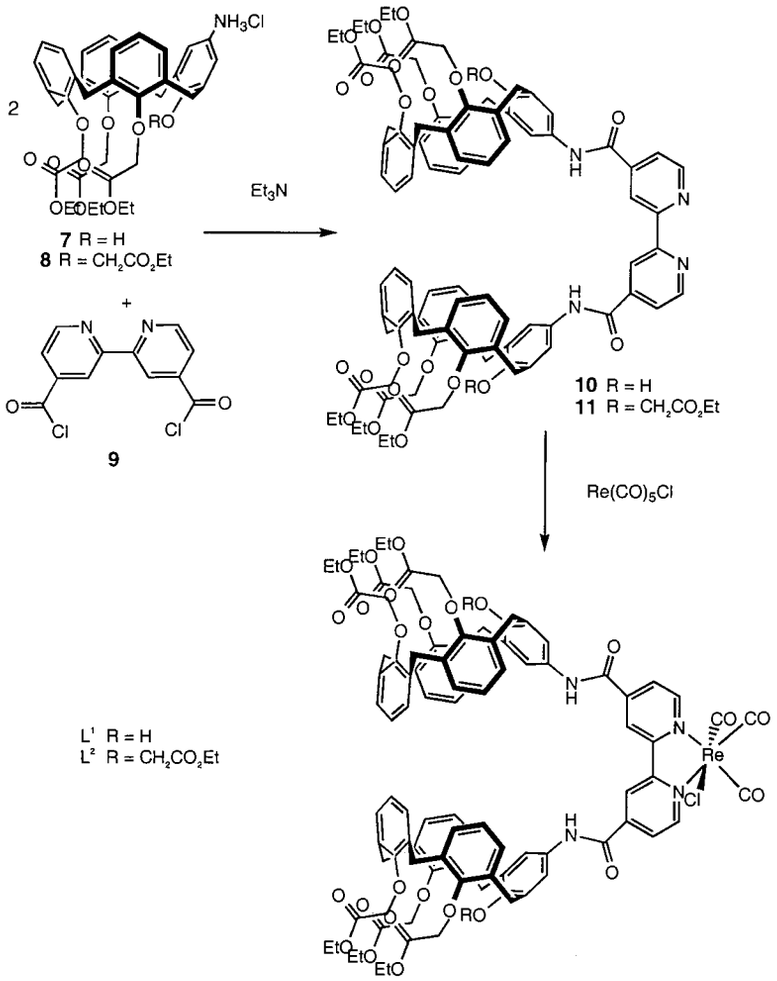
methylene groups and from rings 1 to 4, respectively, these are 45.2(1), 63.8(1), 56.3(1), 79.8(1)° in **4**; 39.6(1), 76.8(1), 37.8(1), 86.7(1)° in **5** and 103.7(1), 30.4(1), 103.3(1), 39.2(1)° in **6**. In **4** the smallest intersection angle involves the unsubstituted phenyl ring from which the hydroxide O(150) forms a hydrogen bond with O(250) at 2.77(1) Å. In **5** the calix[4]arene is slightly more distorted than that in **4**, but again the unsubstituted O(150) forms a hydrogen bond with O(250) of 2.77(1) Å at the lower rim of the calixarene. The distortion towards C_2 symmetry is more pronounced in **6** as phenyl rings 1 and 3 now converge at the upper rim. The shortest O···O distance between adjacent substituted rings at the bottom of the rim is 3.32(1) Å. The lack of hydrogen bond formation and steric crowding at the bottom rim is probably responsible for the more distorted structure.

Receptor syntheses

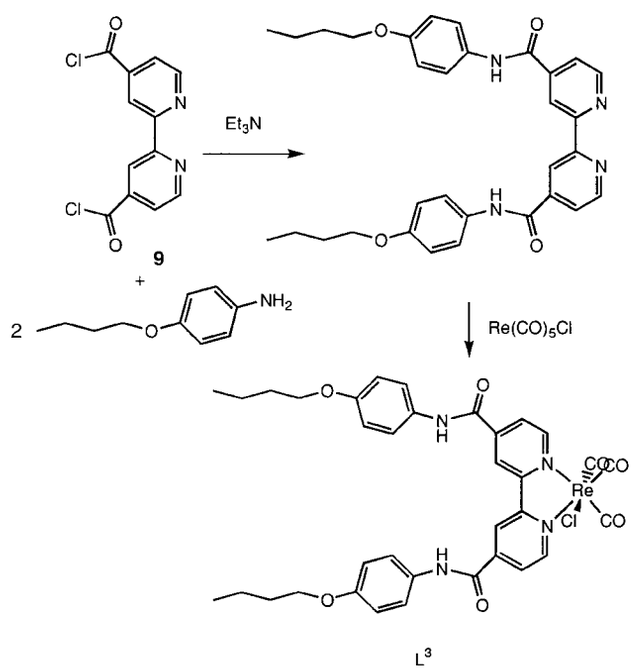
Condensation reactions of 2 equivalents of **7** and **8** with 4,4′-bis(chlorocarbonyl)-2,2′-bipyridine **9**[15] afforded the bis-calix[4]arene-2,2′-bipyridyl linked derivatives **10** and **11** in very good yields. Complexation reactions with $Re(CO)_5Cl$ gave the new receptors L^1 and L^2 as orange and yellow solids in 64 and 45% yields, respectively (Scheme 2). The 'model' non-calix[4]arene receptor L^3 was prepared from **9** and *p*-butoxyaniline followed by complexation with $Re(CO)_5Cl$ (Scheme 3). In an analogous reaction the condensation of 1,1′-bis(chlorocarbonyl)ferrocene **12**[16] with 2 equivalents of **8** produced L^4 in surprisingly low yields of 20–25% (Scheme 4). All these new receptors were characterised by ^1H NMR spectroscopy, FAB mass spectrometry and elemental analysis (see Experimental section).

Anion co-ordination studies

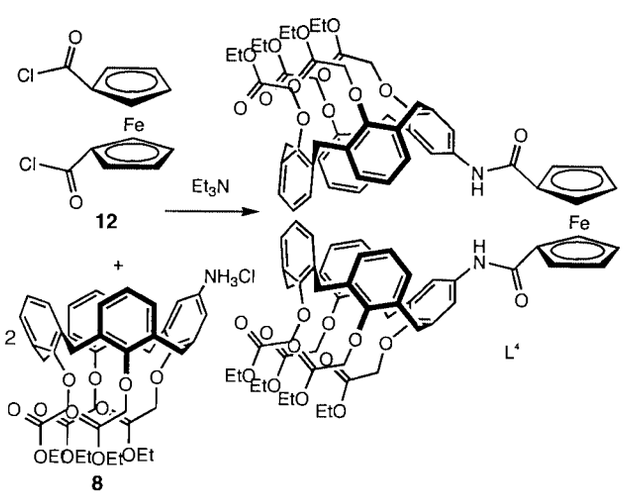
Proton NMR titrations. Proton NMR titration experiments were carried out in deuterated acetonitrile and dimethyl sulfoxide solutions with L^1, L^2 and L^3 and various tetrabutylammonium anion salts. Typically large downfield shifts of the amide, bipy-H_3 and *ortho*-aromatic calixarene protons were observed following the addition of anions, of up to $\Delta\delta = 3.92$ ppm for the amide protons with L^2 and $H_2PO_4^-$ in CD_3CN, which indicates that anion binding is taking place at the upper-rim bis(calix[4]arene) vicinity of receptors L^1 and L^2 (Fig. 4). EQNMR[20] analysis of the resulting titration curves gave stability constant values for 1:1 solution anion complexes shown in Table 2. With both L^1 and L^2, the chloride and benzoate complexes in acetonitrile are so strong in CD_3CN that only a semi-quantitative estimate of the value of K ($> 10^4$ dm^3 mol^{-1}) can be made. It is noteworthy from Table 2 that the presence of the calix[4]arene moieties in receptors L^1 and L^2 has a profound effect on the strength and selectivity of anion binding. The non-calixarene receptor L^3 displays a selectivity preference for acetate over $H_2PO_4^-$ whereas L^2 exhibits the opposite selectivity trend. The relatively harder acetate and chloride anions show the greatest proportional decrease in binding strength due to the presence of the calix[4]arene moieties. The more diffuse benzoate anion displays a much less dramatic decrease in stability constant value. The topological cavity formed by the calixarene moieties may be influencing the anion binding selectivity



Scheme 2



Scheme 3



Scheme 4

in several ways, by creating a sterically hindered environment, and one in which the solvation requirements of an anion are perturbed in a unique fashion. Analogous ^{1}H NMR titration experiments were carried out with the bis(calix[4]arene)-ferrocene receptor L^4 in CD_3CN solutions and the EQNMR [20] determined stability constant values are shown in Table 3. In comparison to L^1 and L^2 Table 3 reveals that L^4 binds anions more weakly, the stability constant magnitudes are smaller than even those determined for L^1 and L^2 in the more polar and competitive DMSO solvent. This observation can be rationalised on the basis of preorganisation, the two cyclopentadienyl rings of the ferrocene receptor L^4 rotate freely about the metal axis and consequently the amide groups are less preorganised to cooperatively coordinate an anionic guest species. In addition the separation distance between the two amide groups of the respective receptors may also be of importance. Interestingly, in contrast to the rhenium receptors, L^4 displays a selectivity preference for benzoate over acetate.

Table 2 Anion stability constant data for L^1, L^2 and L^3 in deuterated DMSO

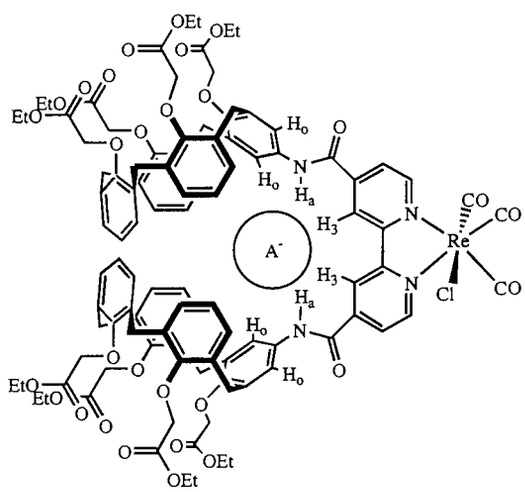
Anion	K^a/dm^3 mol^{-1}		
	L^1	L^2	L^3
$MeCO_2^-$	455	560	845
$PhCO_2^-$	120	120	150
Cl^-	20	20	35
$H_2PO_4^-$	ppt[b]	695	385

[a] Determined at 298 K; errors estimated to be ≤5%. [b] ppt = Precipitate formed during titration and so *K* could not be calculated.

Table 3 Anion stability constant data for L^4 in CD_3CN

Anion	K[a]/dm^3 mol^{-1}
$MeCO_2^-$	135
$PhCO_2^-$	200
Cl^-	35
Br^-	10
I^-	Weak[b]

[a] Determined at 298 K; errors estimated to be ≤ 5%. [b] Very weak binding, a stability constant value could not be calculated in this solvent.



Anion	Δδ/ppm		
	H_a	H_3	H_o
Cl^-	2.14	1.83	0.85
$PhCO_2^-$	3.78	1.13	0.49
$H_2PO_4^-$	3.92	1.36	0.85

Fig. 4 Proposed anion binding site of L^2 and the magnitudes of maximum downfield perturbations Δδ/ppm of amide, bipyridyl and *ortho*-aromatic protons in CD_3CN on anion addition.

Electrochemical anion recognition studies of L^4. The electrochemical properties of L^4 were investigated by cyclic voltammetry in acetonitrile with NBu_4BF_4 as supporting electrolyte. L^4 exhibited a quasi-reversible one-electron oxidation wave at $E_{pa} = 0.50$ V, $E_{pc} = 0.42$ V corresponding to the ferrocene/ferrocenium redox couple. Cyclic voltammograms were also recorded after progressively adding stoichiometric equivalents of anion guests to the electrochemical solutions of L^4 and the results are summarised in Table 4. In all cases upon addition of anions the ferrocene oxidation potential E_{pa} was observed to significantly shift by up to $\Delta E_{pa} = 155$ mV with acetate to more cathodic potentials (Table 4) while the reduction wave E_{pc} disappeared. As noted previously with simple acyclic amide substituted ferrocene derivatives[11,21] this anion induced cathodic perturbation can be attributed to the complexation of an anionic guest close to the ferrocene group

Table 4 Electrochemical anion recognition data[a]

Anion	ΔE_{pa}[b]/mV
$MeCO_2^-$	155
$PhCO_2^-$	120
Cl^-	80
Br^-	55

[a] Cyclic voltammograms recorded in acetonitrile solutions containing 0.2 mol dm^{-3} NBu_4PF_6 as supporting electrolyte. Solutions were *ca.* 1×10^{-3} mol dm^{-3} in L^4 and potentials were obtained with reference to a Ag–Ag$^+$ electrode at 293 K, scan rate = 100 mV s^{-1}. [b] Cathodic shift of oxidation potential produced by the presence of anions (up to 5 equiv.) added as their tetrabutylammonium salts in acetonitrile.

facilitating its oxidation. The disappearance of the reduction wave on anion addition indicates that a bound anion–ferrocenium cation ion pair may be disfavouring reduction back to ferrocene or that an EC mechanism is in operation where after the electron transfer of the oxidation, a chemical process occurs which prevents reduction from being observed. Similar electrochemical anion recognition behaviour has been observed with alkyl and aryl amide substituted ferrocene receptors.[11,21,22]

Proton NMR alkali metal cation and iodide anion binding studies. Receptors L^1, L^2 and L^4 are designed to simultaneously bind cations and anions such that the presence of co-bound alkali metal cations would enhance the strength of anion binding *via* favourable electrostatic interactions and preorganisation effects. Taking into account the known alkali metal cation coordination properties of lower rim ester functionalised calix[4]arenes,[12] that is the metal cation needs to be complexed as strongly as possible to minimise competing ion pairing interactions, and receptor–alkali metal salt solubility considerations, the cation and anion coordination properties of L^1, L^2 and L^4 receptors were investigated by ^{1}H NMR titration experiments in CD_3CN solution. The addition of $LiClO_4$, $NaClO_4$ and KPF_6 salts typically caused the lower rim calixarene ester methylene receptors' protons to initially broaden and sharpen again after 2 equiv. suggesting complexes of $2M^+$:L stoichiometry are being formed in solution, with the alkali metal cations coordinated at the lower rim ester recognition sites.† As a consequence of receptors L^1 and L^2 binding chloride and benzoate anions so strongly in CD_3CN this negated the repetition of ^{1}H NMR titrations in the presence of alkali metal cations. Analogous iodide anion ^{1}H NMR titrations in the absence, using the tetrabutylammonium salt, and presence of 2 equivalents of alkali metal cation, were however undertaken and the EQNMR[20] determined stability constant values are presented in Table 5. Clearly Table 5 shows that with both receptors there is a significant increase in the strength of iodide binding when the alkali metals are co-bound by nearly an order of magnitude in the case of L^2 and sodium cations. This positive cooperative binding of the iodide anion may be attributed to each lower rim ester complexed metal cation rigidifying the calix[4]arene structure in such a way as to preorganise the upper rim for anion binding. Also mutual electrostatic metal cation–anion attraction and through bond inductive electrostatic effects of the complexed metal cation may enhance the relative acidity of the receptors' amide protons leading to stronger hydrogen bonding with the iodide guest anion. The relative magnitudes of this positive cooperative iodide binding effect may be rationalised by considering the structural differences between the two receptors and competing ion pairing effects. It is likely that the lower rim triester receptor L^1 forms compar-

† No evidence for binding of tetrafluoroborate, perchlorate or hexafluorophosphate anions was observed on addition of these tetrabutylammmonium salts to solutions of the receptors.

Table 5 Stability constants for iodide binding in the presence and absence of alkali metal cations in CD_3CN

Receptor	Metal cation[a]	K^b/M^{-1}	Relative enhancement[c]
L^1	None	65	
L^1	Li^+	295	4.5
L^1	Na^+	200	3.1
L^1	K^+	100	1.5
L^2	None	40	
L^2	Li^+	305	7.6
L^2	Na^+	320	8.0
L^2	K^+	210	5.3

[a] Titration carried out in the presence of 2 equiv. of alkali metal cation salt, perchlorates for lithium, sodium and hexafluorophosphate for potassium. [b] Determined at 298 K; errors estimated to be ≤ 5%. [c] Relative anion binding enhancement, $K(M^+)/K$(free receptor) ratio.

Table 6 Stability constants for iodide and bromide binding with L^4 in the presence and absence of sodium and lithium metal cations in CD_3CN

Anion	Metal cation[a]	$K^b/dm^2\ mol^{-1}$	Relative enhancement[c]
I^-	None	weak[d]	
I^-	Li^+	40	
I^-	Na^+	30	
Br^-	None	10	
Br^-	Li^+	133	13.3

[a] Titration carried out in the presence of 2 equivalents of alkali metal cation perchlorate. [b] Determined at 298 K; errors estimated to be ≤ 5%. [c] Relative anion binding enhancement, $K(M^+)/K$(free receptor) ratio. [d] Very weak binding, a stability constant could not be determined.

atively less thermodynamically stable alkali metal cation complexes than the tetraester receptor L^2. Therefore 'free' alkali metal cation–iodide anion ion pairing interactions would compete more effectively for iodide anion binding with receptor L^1 than with L^2 and this leads to lower halide anion binding enhancements (Table 5). It is no coincidence therefore that L^2 exhibits the largest positive cooperative iodide anion binding effect with the sodium cation, which is known to form highly stable and selective complexes with lower rim tetrasubstituted ethyl ester calix[4]arenes.[12] The degree of enhancement of iodide anion binding is thus controlled by the alkali metal cation binding strength of the lower rim.

The results of simultaneous cation and anion binding studies with L^4 are shown in Table 6. In the absence of alkali metals L^4 forms very weak complexes with both bromide and iodide anions. Comparatively large and significant positive cooperative halide binding effects were noted in the presence of lithium and sodium cations, the co-bound alkali metal cation essentially 'switches on' anion binding.[23] Interestingly electrochemical bromide anion recognition experiments revealed a greater than two-fold increase in the magnitude of cathodic shift of the receptors ferrocene redox couple results in the presence of 2 equivalents of lithium cations (ΔE_{pa} = 130 mV) as compared to ΔE_{pa} = 55 mV in the alkali metal's absence.

Conclusions

New heteroditopic bis(calix[4]arene)rhenium(I) bipyridyl (L^1, L^2) and ferrocene receptor (L^4) molecules that have the capability to complex anions at the upper rim and alkali metal cations at the lower rim have been prepared. Proton NMR anion titration studies in deuterated DMSO have shown L^1 and L^2 to bind a variety of anions with selectivity preferences different from that of a non-calixarene analogue. The selectivity and strength of anion binding was also shown to depend on the nature of the calix[4]arene bridging group with the ferrocene containing receptor L^4 binding much more weakly than its rhenium(I) bipyridyl analogue. The presence of lower rim ester functionalised calix[4]arene alkali metal cation binding sites enabled the simultaneous binding of cations and anions to be investigated. With L^1 and L^2 co-bound lithium, sodium and potassium cations were observed to significantly enhance the strength of iodide binding in acetonitrile solutions. The greatest positive cooperative iodide binding effect was noted with L^2 and co-bound sodium cations which correlates with the known lower rim tetrasubstituted ethyl ester selectivity preference for this alkali metal cation. Large iodide and bromide binding enhancements were also displayed by L^4 in the presence of lithium and sodium cations, with the former cation amplifying the electrochemical response of L^4 to bromide anions.

Acknowledgements

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