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Potassium cation cooperative anion recognition by heteroditopic calix[4]arene bis(benzo-15-crown-5) receptor molecules

Andrew J. Evans and Paul D. Beer *
Department of Chemistry, Inorganic Chemistry Laboratory, University of Oxford, South Parks Road, Oxford, UK OX1 3QR. E-mail: paul.beer@chem.ox.ac.uk

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New upper-rim functionalised heteroditopic calix[4]arene receptors containing amide linked bis(benzo-15-crown-5) ether, bis(benzo-15-crown-5)-bis(ferrocene) and tetrakis(benzo-15-crown-5) groups have been prepared. ^{1}H NMR titration studies reveal the bis(benzo-15-crown-5) potassium cation complexed calix[4]arene receptors enhance the strength of chloride, benzoate and dihydrogen phosphate binding in polar organic solvents *via* favourable preorganisation and electrostatic effects. Cyclic and square wave voltammetric investigations demonstrate that the bis(ferrocene) containing calix[4]arene receptor is capable of electrochemical anion recognition. In the presence of potassium cations the electrochemical response to benzoate anions was amplified significantly.

Introduction

The design of new heteroditopic ligands for the simultaneous complexation of anionic and cationic guest species (ion-pair recognition) is a new, emerging and topical field of coordination chemistry.[1] These multisite ligands can increase the lipophilicity of ionic guests and therefore enhance ion-pair solubility in non-polar media, leading to their exploitation in both extraction and membrane transport systems.[2] In addition, ion-pair receptors are capable of coordinating important biological molecules such as zwitterionic amino acids and peptides.[3]

Lewis acidic groups, hydrogen bonding or positively charged centres to coordinate the anion, covalently linked to crown ether or modified calixarenes to complex the cation, have produced heteroditopic receptors which frequently exhibit cooperative and allosteric binding behaviours. The cooperativity can be positive or negative depending upon whether the association of one ion respectively enhances or reduces the binding strength of the counter ion.[4] Several factors can be responsible for cooperative binding behaviour such as through-bond or through-space electrostatic interactions between bound ions or conformational changes induced by complexation. We report here new amide linked bis(benzo-15-crown-5) ether and bis-(benzo-15-crown-5)-bis(ferrocene) upper-rim functionalised heteroditopic calix[4]arene receptors which on potassium cation complexation cooperatively bind chloride, benzoate and dihydrogen phosphate anions.

Results and discussion

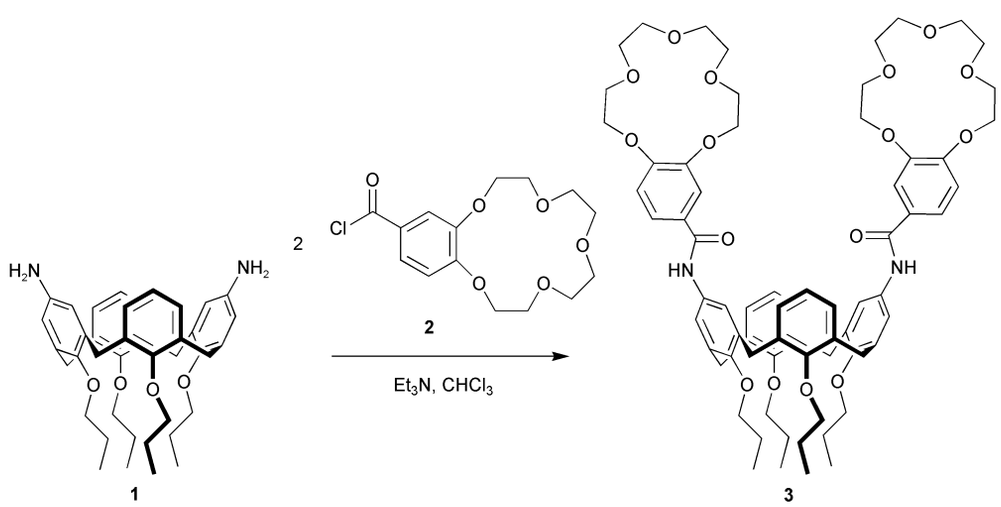
Synthesis

The regioselective upper-rim functionalisation of the calix-[4]arene framework was exploited in the construction of a novel series of heteroditopic multisite receptors containing amide linked benzo-15-crown-5 ether and ferrocene moieties (Schemes 1–3).

The condensation[5] of the 1,3-bis(amino) calix[4]arene derivative **1**[6] with two equivalents of 4-(chlorocarboxy)benzo-15-crown-5 **2**[7] in chloroform in the presence of triethylamine base gave the new bis(benzo-15-crown-5) upper-rim functionalised calix[4]arene receptor **3** in 63% yield (Scheme 1).

Selective Boc protection of the tetrakis(amino) calix[4]arene compound **4**[8] afforded **5** which on condensation with two equivalents of chlorocarbonyl ferrocene **6**[9] produced **7** in 81% yield. Deprotection with TFA (trifluoroacetic acid) followed by addition of two equivalents of **2** gave the mixed ferrocene/benzo-15-crown-5 upper-rim functionalised calix[4]arene receptor **8** in 49% yield (Scheme 2).

The condensation of four equivalents of **2** with **4** in chloroform in the presence of triethylamine base produced the tetrakis(benzo-15-crown-5) calix[4]arene receptor **9** in 57% isolated yield (Scheme 3). All these new receptors were characterised by ^{1}H NMR spectroscopy, electrospray mass spectrometry and elemental analysis (see Experimental section).



Scheme 1

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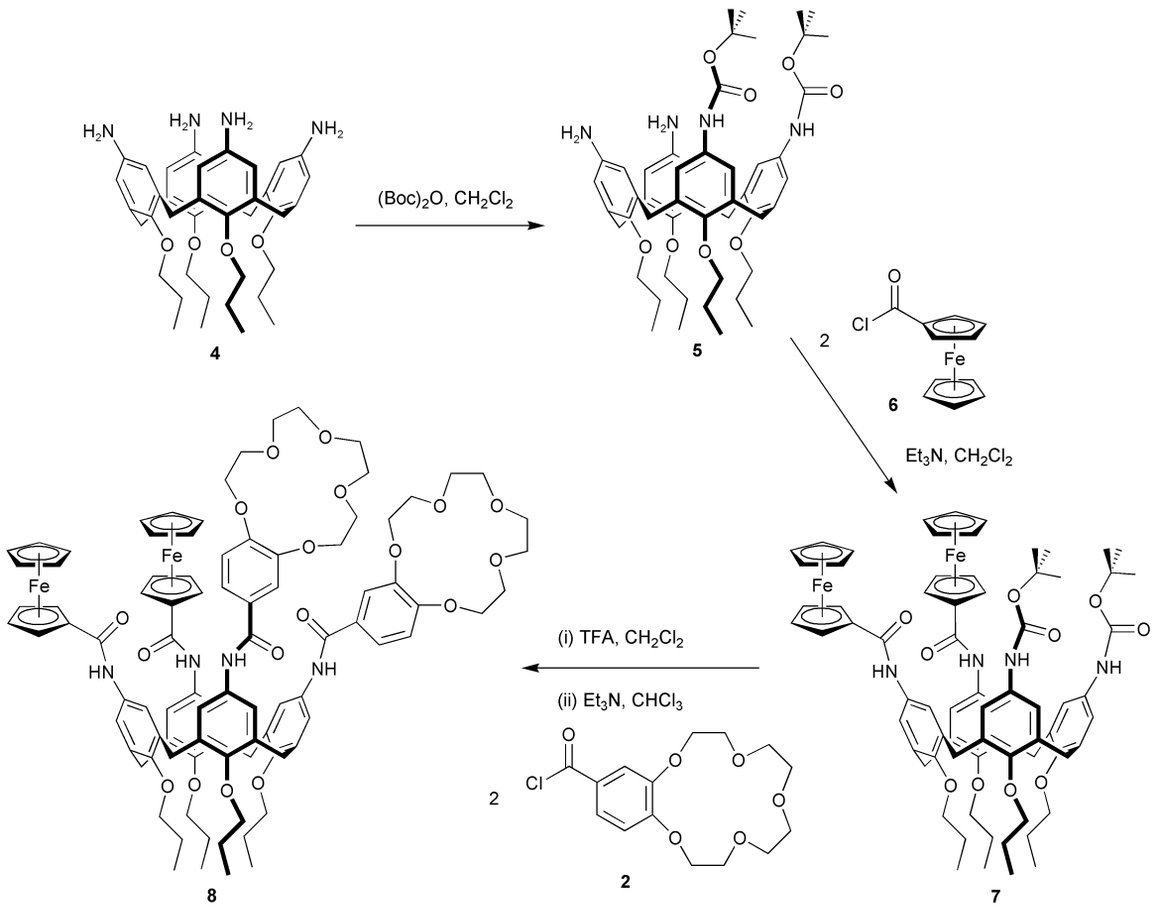
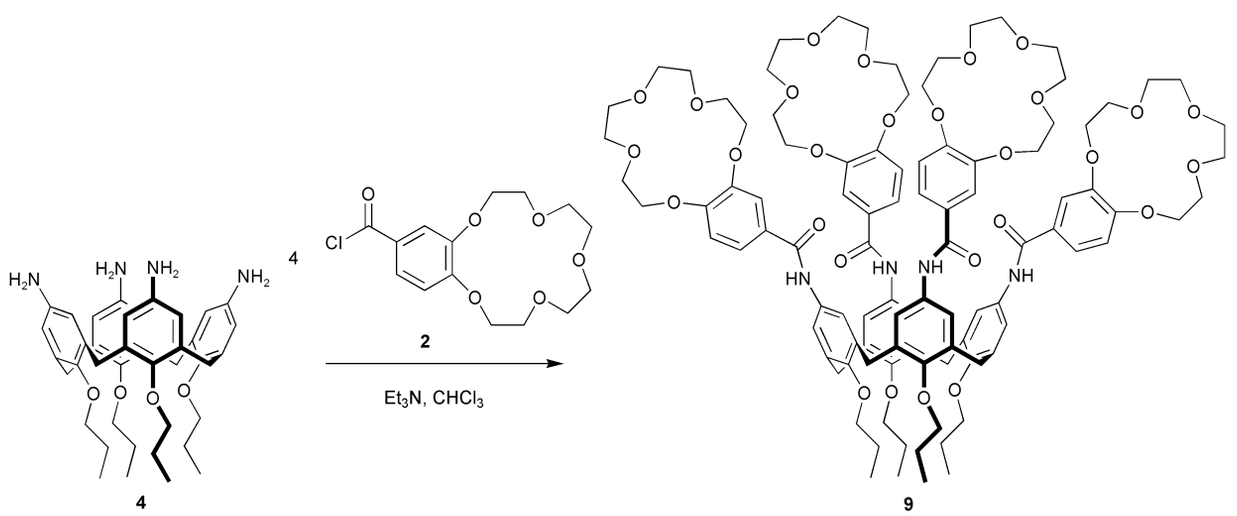


Scheme 2



Scheme 3

^{1}H NMR binding studies

Receptors **3**, **8** and **9** were 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. Titration experiments were conducted with **3**, **8** and **9** with chloride, benzoate and dihydrogen phosphate anions, added as their tetrabutylammonium salts, both in the absence and presence of equivalents of sodium and potassium cations, added as their perchlorate salts. The choice of solvent for these experiments was limited because all possible species that might exist in the titration experiment (receptor, ion-pair salts, cation–anion–receptor complexes) need to be soluble in the selected solvent. Also, ideally the metal cation must be bound strongly so as to minimise ion-pairing outside of the receptor. Taking this into account, the cation and anion coordination properties of **3**, **8** and **9** were investigated by ^{1}H NMR titration experiments in 1 : 1 CD_3CN : d_6-DMSO (in the majority of cases).

The addition of $NaClO_4$ and $KClO_4$ salts caused significant upfield perturbations of the crown ether OCH_2 signals in the respective ^{1}H NMR spectra. Notably, addition of K^+ also resulted in an upfield shift in the amide resonances due to complexation-induced conformational effects. Stability constant values could not be determined however, as it proved impossible to continually monitor a specific signal throughout the titration experiment.

Electrospray mass spectrometry (ESMS) results with excess sodium cations gave predominant receptor–alkali metal

Table 1 Anion stability constant data for receptors (errors ≤ 10 %)

	3	8	9
Cl^- [a]	5	25	10
+ 2 Na^+	< 5	< 5	< 5 [d]
+ K^+	15	150	15 [e]
OBz^- [a]	25	105	30
+ 2 Na^+	< 5	20	< 5 [d]
+ K^+	270	205	30 [e]
$H_2PO_4^-$ [b]	10	80	[c]
+ 2 Na^+	< 5	< 5	< 5 [d]
+ K^+	60	[c]	[c]

[a] Titrations carried out in 1 : 1 CD_3CN : d_6-DMSO. [b] Titrations carried out in 100% d_6-DMSO. [c] EQNMR unable to fit data. [d] 4 equivalents of Na^+. [e] 2 equivalents of K^+.

complex species where the Na^+ was bound in each of the benzo-15-crown-5 moieties of the respective receptor. Analogous ESMS experiments with potassium cations revealed 1 : 1 intramolecular sandwich complex species as the major molecular ions with receptors **3** and **8**. Bis(benzo-15-crown-5) ether ligands are well known to form sandwich complexes with potassium cations.[10] Interestingly, ESMS competition experiments of **3** with five equivalents each of Li^+, Na^+, K^+, Rb^+ and Cs^+ in acetonitrile solutions revealed $[\mathbf{3} + K]^+$ as the most intense singularly charged molecular species and $[\mathbf{3} + 2Na]^{2+}$ as the most prominent doubly charged species.

Stability constant values for anion binding in the presence/absence of Na^+ (one equivalent $NaClO_4$ per benzo-15-crown-5 group of the respective receptor) and K^+ (0.5 equivalents $KClO_4$ per crown ether) were determined by EQNMR [11] analysis of the titration curves, monitoring the amide protons of the respective receptor (Fig. 1). In the case of dihydrogen phosphate, precipitation problems necessitated titration experiments being undertaken in 100% d_6-DMSO. As Table 1 shows, all three receptors bind anions with modest stability constant values of up to $K = 105\ M^{-1}$ with **8** and benzoate, reflecting its greater basicity. The more acidic ferrocenoyl amide protons present in **8** may account for this receptor forming stronger anion complexes than **3** and **9**.

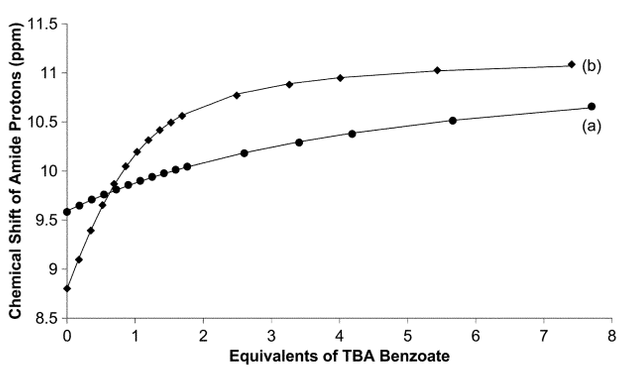


Fig. 1 ^1H NMR titration curves for (a) **3** and (b) **3**·K^+ upon addition of benzoate anions in 1 : 1 CD_3CN : d_6-DMSO.

It is noteworthy that with the bis crown ether calix[4]arene receptors **3** and **8** the presence of one equivalent of K^+ results in a significant increase in the strength of chloride, benzoate and dihydrogen phosphate binding by up to an order of magnitude in the case of **3** and benzoate. In contrast, with two equivalents of Na^+ a general decrease in the strength of anion binding is observed. These observations may be rationalised by the fact that K^+ forms a 1 : 1 intramolecular sandwich complex with the benzo-15-crown-5 ether moieties of **3** and **8** which in effect preorganises the amide groups for anion binding (Fig. 2 (a)). Also mutual electrostatic potassium 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 guest anion. In contrast, the $2Na^+$: 1 receptor stoichiometry with sodium, in which each crown ether complexes Na^+, results in the amides being unable to cooperatively complex an anion due to mutual repulsive sodium cation crown ether electrostatic effects (Fig. 2 (b)). Similar results were noted with the tetra-crown derivative **9** and four equivalents of sodium. Interestingly, little difference in binding strength of benzoate anions was observed in the presence of one or two equivalents of potassium cations.

Table 2 Cathodic shifts in E_{pa} values [a] (mV) of **8** upon addition of five equivalents of anions, for the free receptor and in the presence of one equivalent of $KClO_4$

	8	[8·K^+]
Cl^-	50	60
OBz^-	30	75
$H_2PO_4^-$	170	165

[a] Conditions: 5×10^{-4} M solutions of **8** in 0.1 M tetrabutylammonium tetrafluoroborate in 1 : 1 CH_2Cl_2 : CH_3CN, glassy carbon working electrode, Pt auxilliary electrode, $Ag/AgNO_3$ reference electrode. CVs recorded with a scan rate of 100 mV s^{-1}. SWVs recorded with a scan increment of 2 mV and a frequency of 25 Hz. Errors ± 10 mV.

Electrochemical anion recognition studies of 8

The electrochemical properties of **8** were investigated by cyclic and square wave voltammetry in 1 : 1 CH_2Cl_2/CH_3CN with tetrabutylammonium tetrafluoroborate as supporting electrolyte. The receptor exhibited a quasi-reversible two-electron oxidation wave at E_{pa} = 259 mV and E_{pc} = 166 mV (*vs.* Ag/ $AgNO_3$ reference) which suggests the two ferrocene moieties behave independently of one another and are oxidised at the same potential. Voltammograms were also recorded after progressively adding stoichiometric equivalents of anionic guests to the electrochemical solutions of **8** and the results are summarised in Table 2. In all cases, upon addition of anions the ferrocenes' oxidation potential E_{pa} was observed to significantly shift by up to ΔE_{pa} = 170 mV with dihydrogen phosphate to more cathodic potentials (Table 2) while the reduction wave E_{pc} disappeared. As noted previously with simple acyclic amide substituted ferrocene derivatives [12] this anion induced cathodic perturbation can be attributed to the complexation of an anionic guest close to the ferrocene moieties facilitating their 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 reaction process occurs which prevents reduction from being observed. Similar electrochemical anion recognition behaviour has been observed with alkyl and aryl amide substituted ferrocene receptors.[12] Whereas with chloride and benzoate a gradual shifting redox wave is noted, with dihydrogen phosphate the appearance of a new wave is seen which suggests the binding of this anion is kinetically slow on the CV or SWV timescale. Interestingly, in the presence of one equivalent of $KClO_4$ the magnitude of the cathodic shifts increased significantly to ΔE_{pa} = 75 mV for benzoate, whereas little difference was noted with chloride and dihydrogen phosphate.

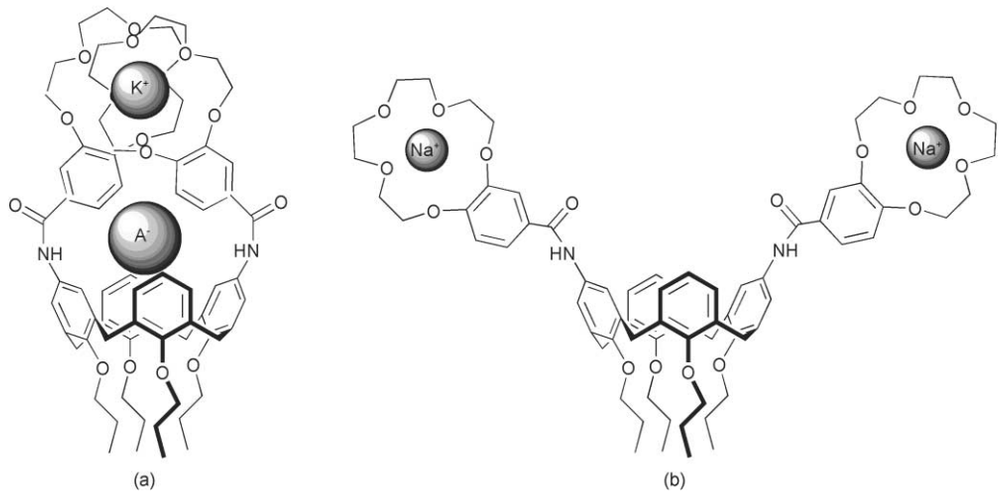


Fig. 2 Schematic representation of (a) 1 : 1 potassium cation sandwich complex of **3** favouring anion complexation and (b) $2Na^+$: **3** complex which is unable to cooperatively bind an anion.

Solid/liquid extraction studies

The ability of receptor **3** to extract and solubilise various sodium and potassium salts into non-polar organic solvents was investigated. In a typical experiment, the receptor was dissolved in $CDCl_3$ and stirred with an excess of solid KCl, KOAc, KH_2PO_4, NaCl, NaOAc or NaH_2PO_4 for 24 hours. After filtration, the ^{1}H NMR spectra were recorded and compared to that of the free receptor. No changes were observed in the ^{1}H NMR spectra except in the case of KOAc. After extraction, the spectrum revealed the amide proton of the receptor was shifted downfield by 2.8 ppm and a peak corresponding to the acetate anion had appeared at 1.99 ppm. Integration of this signal indicates that **3** extracts KOAc with 100% efficiency.

Conclusion

A series of new amide linked bis(benzo-15-crown-5), bis(ferrocene)-bis(benzo-15-crown-5) and tetrakis(benzo-15-crown-5) upper-rim functionalised heteroditopic calix[4]arene receptor molecules have been prepared. ^{1}H NMR titration studies reveal the bis(benzo-15-crown-5) potassium cation intramolecular sandwich complexed calix[4]arene receptors **3** and **8** enhance significantly the strength of chloride, benzoate and dihydrogen phosphate anion binding *via* favourable preorganisation and electrostatic effects. In contrast, negative cooperative binding effects are observed with co-bound sodium cations. Electrochemical investigations reveal the bis(ferrocene) containing receptor **8** to electrochemically recognise anions, with the presence of potassium cation amplifying the magnitude of the cathodic electrochemical response of **8** to benzoate.

Experimental

General

Unless otherwise stated, commercial grade solvents and other chemicals were used without further purification. Dry solvents were used for some syntheses and all electrochemical studies; dichloromethane and acetonitrile were dried by distillation over calcium hydride. Tetrabutylammonium salts of chloride, benzoate and dihydrogen phosphate were stored in a desiccator under vacuum containing self-indicating silica. 1,3-Bis(amino) calix[4]arene derivative **1**,[6] 4-(chlorocarboxy)benzo-15-crown-5 **2**,[7] tetrakis(amino) calix[4]arene compound **4**,[8] 1,2-di(Boc-protected) calix[4]arene derivative **5**[8] and chlorocarbonyl ferrocene **6**[9] were prepared according to literature procedures.

NMR spectra were recorded on a Varian Mercury 300 or a Varian Unity Plus 500 instrument. Elemental analyses[13] and electrospray mass spectrometry were performed by in-house services at the Inorganic Chemistry Laboratory, University of Oxford. FAB mass spectometry was performed by the EPSRC mass spectrometry service, University of Wales, Swansea.

Syntheses

Bis(benzo-15-crown-5) upper-rim functionalised calix[4]arene receptor 3. A solution of the 1,3-bis(amino) calix[4]arene derivative **1** (220 mg, 0.35 mmol) in chloroform (50 mL) was added dropwise to a stirred solution of 4-(chlorocarboxy)benzo-15-crown-5 **2** (350 mg, 1.06mmol) and triethylamine (2 mL, excess) in chloroform (50 mL) and the mixture heated to reflux under nitrogen overnight. The heat was removed and aqueous lithium hydroxide (1 M, 50 mL) added and the solution stirred at room temperature overnight. The organic layer was separated, washed with water (50 mL), dried over anhydrous magnesium sulfate, filtered and the solvent removed under vacuum. The product was obtained as a white solid after precipitation from chloroform/hexane (270 mg, 63%) (Found: C, 68.2; H, 6.8; N, 2.3%. $C_{70}H_{86}N_2O_{16}$ requires C, 69.4; H, 7.2; N, 2.3%). ES-MS *m*/*z*: 1249.8 (MK^+, 100 %). ^{1}H NMR (500 MHz, d_6-DMSO): δ 9.85 (s, N*H*, 2H), 7.58 (d, J = 8.5 Hz, benzoAr*H*, 2H), 7.54 (s, benzoAr*H*, 2H), 7.40 (s, Ar*H*, 4H), 7.02 (d, J = 8.5 Hz, benzoAr*H*, 2H), 6.38 (m, Ar*H*, 6H), 4.36 (d, J = 13.0 Hz, $ArCH_{ax}H_{eq}Ar$, 4H), 4.10 (s, $ArOCH_2CH_2O$, 8H), 3.90 (t, J = 7.5 Hz, $OCH_2CH_2CH_3$, 4H), 3.78 (s, $ArOCH_2CH_2O$, 8H), 3.67 (t, J = 7.5 Hz, $OCH_2CH_2CH_3$, 4H), 3.61 (s, OCH_2CH_2O, 16H), 3.12 (d, J = 13.0 Hz, $ArCH_{ax}H_{eq}Ar$, 4H), 1.94 and 1.86 (both sext, J = 7.5 Hz, $OCH_2CH_2CH_3$, 2 × 4H), 1.03 and 0.89 (both t, J = 7.5 Hz, $OCH_2CH_2CH_3$, 2 × 6H).

1,2-Bis(ferrocene) upper-rim functionalised calix[4]arene 7. A solution of the 1,2-di(Boc-protected) calix[4]arene derivative **5** (990 mg, 1.16 mmol) in dry dichloromethane (50 mL) was added dropwise to a stirred solution of chlorocarbonyl ferrocene **6** (870 mg, 3.50 mmol) and triethylamine (5 mL, excess) in dry dichloromethane (50 mL) and the mixture was stirred for 48 hours under a nitrogen atmosphere. Water (100 mL) was added and the mixture stirred for 30 minutes. The organic fraction was separated, washed with water (100 mL), dried over anhydrous magnesium sulfate, filtered, and the solvent removed under vacuum. The product was obtained as a pale orange powder after precipitation from chloroform/hexane, followed by filtration and washing with hexane (1200 mg, 81%) (Found: C, 67.2; H, 6.6; N, 4.4%. $C_{72}H_{84}Fe_2N_4O_{10}$ requires C, 67.7; H, 6.6; N, 4.4%). FAB-MS *m*/*z*: 1078.3 ($M - 2(BOC)H^+$, 100 %), 1178.3 ($M - (BOC)H^+$, 55 %), 1278.3 (MH^+, 20 %). ^{1}H NMR (300 MHz, d_6-DMSO): δ 9.14 (s, FcN*H*, 2H), 8.77 (s, BOCN*H*, 2H), 7.09 and 7.04 and 6.85 and 6.81 (all s, Ar*H*, 4 × 2H), 4.90

(s, C_5H_4, 4H), 4.34 (m, C_5H_4 and Ar$CH_{ax}H_{eq}$Ar, 8H), 4.14 (s, C_5H_5, 10H), 3.81 and 3.76 (both t, J = 7.2 Hz, OCH_2-CH_2CH_3, 2 × 4H), 3.16 and 3.03 (both d, J = 12.9 Hz, $ArCH_{ax}$-H_{eq}Ar, 2 × 1H), 3.09 (d, J = 12.9 Hz, $ArCH_{ax}H_{eq}$Ar, 2H), 1.93 and 1.91 (both sext, J = 7.2 Hz, $OCH_2CH_2CH_3$, 2 × 4H), 1.35 (s, CH_3, 18H), 0.97 (t, J = 7.2 Hz, $OCH_2CH_2CH_3$, 12H).

1,2-Bis(ferrocene)-3,4-bis(benzo-15-crown-5) upper-rim functionalised calix[4]arene receptor 8. Trifluoroacetic acid (TFA, 10 mL, excess) was added to a solution of **7** (600 mg, 0.47 mmol) in dichloromethane (50 mL) and the mixture stirred for 2 hours. The solvent was removed under vacuum and the residue dried under high vacuum for several hours. The residue was dissolved in chloroform (50 mL) and added dropwise to a stirred solution of 4-(chlorocarboxy)benzo-15-crown-5 **2** (480 mg, 1.45 mmol) and triethylamine (2 mL, excess) in chloroform (50 mL) and the mixture heated to reflux under nitrogen overnight. The heat was removed and aqueous lithium hydroxide (1 M, 50 mL) added and the solution stirred at room temperature overnight. The organic layer was separated, washed with water (50 mL), dried over anhydrous magnesium sulfate, filtered and the solvent removed under vacuum. The product was obtained as a pale orange solid after precipitation from chloroform/hexane (390 mg, 49%) (Found: C, 65.0; H, 6.0; N, 3.5%. $C_{92}H_{104}Fe_2N_4O_{18}$ requires C, 66.3; H, 6.3; N, 3.4%). ES-MS m/z: 856.0 (MNa_2^{2+}, 100 %), 864.0 ($MNaK^{2+}$, 60 %), 1689.1 (MNa^+, 15 %), 1705.0 (MK^+, 15 %). ^{1}H NMR (500 MHz, d_6-DMSO): δ 9.77 (s, benzoNH, 2H), 9.19 (s, FcNH, 2H), 7.49 (d, J = 8.5 Hz, benzoArH, 2H), 7.43 (s, benzoArH, 2H), 7.28 (s, ArH, 2H), 7.20 (s, ArH, 4H), 7.17 (s, ArH, 2H), 6.93 (d, J = 8.5 Hz, benzoArH, 2H), 4.86 (s, C_5H_4, 4H), 4.43 (d, Ar$CH_{ax}H_{eq}$Ar, J = 12.0 Hz, 4H), 4.31 (s, C_5H_4, 4H), 4.14 (s, C_5H_5, 10H), 4.05 and 3.98 (both s, $ArOCH_2CH_2O$, 2 × 4H), 3.85 (t, J = 7.5 Hz, $OCH_2CH_2CH_3$, 8H), 3.74 and 3.68 (both s, $ArOCH_2CH_2O$, 2 × 4H), 3.58 (s, OCH_2CH_2O, 16H), 3.18 (d, J = 12.0 Hz, $ArCH_{ax}H_{eq}$Ar, 4H), 1.96 and 1.94 (both sext, J = 7.5 Hz, $OCH_2CH_2CH_3$, 2 × 4H), 0.97 (t, J = 7.5 Hz, $OCH_2CH_2CH_3$, 12H).

Tetrakis(benzo-15-crown-5) upper-rim functionalised calix[4]-arene receptor 9. Procedure was the same as that for receptor **3** except the tetrakis(amino) calix[4]arene derivative **4** (300 mg, 0.46 mmol) and 4-(chlorocarboxy)benzo-15-crown-5 **2** (910 mg, 2.75 mmol) were used. The product was obtained as a white solid after precipitation from chloroform/hexane (480 mg, 57%) (Found: C, 65.1; H, 7.0; N, 3.1%. $C_{100}H_{124}N_4O_{28}$ requires C, 65.6; H, 6.8; N, 3.1%). ES-MS m/z: 633.1 (MNa_3^{3+}, 50 %), 638.4 (MNa_2K^{3+}, 90 %), 938.1 (MNa_2^{2+}, 70 %), 946.1 ($MNaK^{2+}$, 100 %), 1853.2 (MNa^+, 10 %), 1869.2 (MK^+, 15 %). ^{1}H NMR (500 MHz, d_6-DMSO): δ 9.74 (s, NH, 4H), 7.48 (d, J = 8.5 Hz, benzoArH, 4H), 7.43 (s, benzoArH, 4H), 7.20 (s, ArH, 8H), 6.89 (d, J = 8.5 Hz, benzoArH, 4H), 4.43 (d, J = 12.5 Hz, Ar$CH_{ax}H_{eq}$Ar, 4H), 4.05 and 4.00 (both s, $ArOCH_2CH_2O$, 2 × 8H), 3.84 (t, J = 7.0 Hz, $OCH_2CH_2CH_3$, 8H), 3.75 and 3.71 (both s, $ArOCH_2CH_2O$, 2 × 8H), 3.59 (s, OCH_2CH_2O, 32H), 3.16 (d, J = 12.5 Hz, $ArCH_{ax}H_{eq}$Ar, 4H), 1.93 (sext, J = 7.0 Hz, $OCH_2CH_2CH_3$, 8H), 0.96 (t, J = 7.0 Hz, $OCH_2CH_2CH_3$, 12H).

^{1}H NMR titrations

^{1}H NMR spectra were recorded on a Varian Mercury 300 instrument. In a typical anion titration experiment, aliquots of an anion (tetrabutylammonium chloride, benzoate or dihydrogen phosphate, 0.5 M, 2.5×10^{-4} moles in 0.5 mL deuterated solvent) were added to a 0.5 mL solution of a receptor (0.01 M, 5×10^{-6} moles in 0.5 mL deuterated solvent). Fifteen aliquots were added (10 × 2 μL, 3 × 10 μL, 1 × 20 μL and 1 × 30 μL) corresponding to 0, 0.2, 0.4, 0.6, 0.8, 1, 1.2, 1.4, 1.6, 1.8, 2, 3, 4, 5, 7 and 10 equivalents of anion. The chemical shift of a specific proton on the receptor was monitored as it moved downfield upon addition of anions. The resulting titration data was analysed by the computer program EQNMR[11] to yield stability constants for the anion/receptor binding processes. For titrations in the presence of cations, the above procedure was repeated for addition of anions to a mixture of a receptor (5×10^{-6} moles in 0.4 mL deuterated solvent) and potassium or sodium perchlorate (0.1 mL of a 0.05, 0.1 or 0.2 M solution in deuterated solvent depending on the required receptor/cation stoichiometry).

Electrochemistry

Cyclic voltammetry (CV) and square wave voltammetry (SWV) were performed on a EG & G Princeton Applied Research Potentiostat/Galvanostat model 273 linked to a computer using a National Instruments GPIB-PCII/IIA interface and controlled by EG & G Princeton Applied Research Model 270/250 Research Electrochemistry Software. A standard one-compartment three-electrode electrochemical cell was used with a glassy carbon solid disc working electrode, a platinum wire auxiliary electrode and a silver/silver nitrate reference electrode (silver wire in 10 mM silver nitrate in electrolyte solution). In all experiments, the electrolyte solution was 0.1 M tetrabutylammonium tetrafluoroborate in 1 : 1 dichloromethane/acetonitrile. Ferrocene was employed as an internal standard ($E_{½}$ feroocene = 55 ± 5 mV with respect to the $Ag/AgNO_3$ reference electrode). CVs were typically recorded with a 5 s equilibration time, a scan increment of 2 mV and a scan rate of 100 mV s^{-1}; two cycles were recorded and the second one used for analysis. SWVs were typically recorded with a 5 s equilibration time, a scan increment of 2 mV and a frequency of 25 Hz. The working electrode was cleaned between scans by polishing on a solvent-soaked cloth. Anion sensing studies were performed with the receptor (5×10^{-4} M in electrolyte solution) by recording a CV and SWV after the addition of 0, 0.5, 1, 2, 5, 10 and 20 equivalents of anion (tetrabutylammonium chloride, benzoate or dihydrogen phosphate, 0.125 M in electrolyte solution, 20 μL is 1 equivalent) to a 5 mL aliquot of the receptor solution. Ion-pair sensing studies involved the addition of 1 equivalent of potassium perchlorate (0.125 M in dimethyl sulfoxide, 20 μL is 1 equivalent) to a 5 mL aliquot of the receptor solution prior to performing the anion sensing studies.

Acknowledgements

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References and notes

1 J. E. Redman, P. D. Beer, S. W. Dent and M. G. B. Drew, *Chem. Commun.*, 1998, 231; S. Nishizawa, K. Shigemori and N. Teramae, *Chem. Lett.*, 1999, 1185; P. D. Beer and J. B. Cooper, *Chem. Commun.*, 1998, 129; J. B. Cooper, M. G. B. Drew and P. D. Beer, *J. Chem. Soc., Dalton Trans.*, 2000, 2721; R. Shukla, T. Kida and B. D. Smith, *Org. Lett.*, 2000, **2**, 3099; P. D. Beer and P. A. Gale, *Angew. Chem., Int. Ed.*, 2001, **40**, 486.

2 N. Pelizzi, A. Casnati, A. Friggeri and R. Ungaro, *J. Chem. Soc., Perkin Trans. 2*, 1998, 1307; M. T. Reetz, C. M. Niemeyer and K. Harms, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 1472; M. T. Reetz, B. M. Johnson and K. Harms, *Tetrahedron Lett.*, 1994, **35**, 2525; D. M. Rudkevich, Z. Brzozka, M. Palys, H. C. Visser, W. Verboom and D. N. Reinhoudt, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 467; D. M. Rudkevich, J. D. Mercer-Chalmers, W. Verboom, R. Ungaro, F. de Jong and D. N. Reinhoudt, *J. Am. Chem. Soc.*, 1995, **117**, 6124; P. D. Beer, P. K. Hopkins and J. D. McKinney, *Chem. Commun.*, 1999, 1253; D. J. White, N. Laing, H. Miller, S. Parsons, S. Coles and P. A. Tasker, *Chem. Commun.*, 1999, 2077.

3 K. I. Kinnear, D. P. Mousley, E. Arafa and J. C. Lockhart, *J. Chem. Soc., Dalton Trans.*, 1994, 3637; H. Tsukube, M. Wada, S. Shinoda and H. Tamiaki, *Chem. Commun.*, 1999, 1007; M. A. Hossain and H.-J. Schneider, *J. Am. Chem. Soc.*, 1998, **120**, 11208; P. Breccia, M. V. Gool, R. Perez-Fernandez, S. Martin-Santamaria, F. Gago, P. Prados and J. de Mendoza, *J. Am. Chem. Soc.*, 2003, **125**, 8270.

4 For examples of allosteric behaviour in ion-pair recognition, see J. Scheerder, J. P. M. van Duynhoven, J. F. J. Engbersen and D. N. Reinhoudt, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 1090; P. D. Beer and S. E. Stokes, *Polyhedron*, 1995, **14**, 2631.
5 In all condensation reactions of this type a 1.5 equivalent excess of acid chloride per calix[4]arene amine group was used.
6 A. M. A. van Wageningen, E. Snip, W. Verboom, D. N. Reinhoudt and H. Boerrigter, *Liebigs Ann. Recl.*, 1997, **11**, 2235.
7 A. H. Haines, I. Hodgkisson and C. Smith, *J. Chem. Soc., Perkin Trans. 1*, 1983, **2**, 311.
8 W. Verboom, A. Durie, R. J. M. Egberink, Z. Asfari and D. N. Reinhoult, *J. Org. Chem.*, 1992, **57**, 1313; V. Böhmer, R. A. Jakobi, C. Grüttner, D. Kraft and W. Vogt, *New J. Chem.*, 1996, **20**, 493; M. Saadioui, A. Shivanyuk, V. Böhmer and W. Vogt, *J. Org. Chem.*, 1999, **64**, 3774.
9 P. C. Reeves, *Org. Synth.*, 1978, **56**, 28.
10 P. D. Beer, M. G. B. Drew, R. J. Knubley and M. I. Ogden, *J. Chem. Soc., Dalton Trans.*, 1995, 3117; K. Kikukawa, G.-X. He, A. Abe, T. Goto, R. Arata, T. Ikeda, F. Wada and T. Matsuda, *J. Chem. Soc., Perkin Trans. 2*, 1987, 135; P. D. Beer, E. L. Tite and A. Ibbotson, *J. Chem. Soc., Dalton Trans.*, 1990, 2691; Y. Inoue, T. Hakushi, Y. Liu, L.-H. Tong, J. Hu, G.-D. Zhao, S. Huang and B.-Z. Tian, *J. Phys. Chem.*, 1988, **92**, 2371; S. Shinkai, T. Nakaji, T. Ogawa, K. Shigematsu and O. Manabe, *J. Am. Chem. Soc.*, 1981, **103**, 111.
11 M. J. Hynes, *J. Chem. Soc., Dalton Trans.*, 1993, 311.
12 P. D. Beer, Z. Chen, A. J. Goulden, A. R. Graydon, S. Stokes and T. Wear, *J. Chem. Soc. Chem. Commun.*, 1993, 1834; P. D. Beer, *Chem. Commun.*, 1996, 689; P. D. Beer, A. R. Graydon, A. O. M. Johnson and D. K. Smith, *Inorg. Chem.*, 1997, **36**, 2112; P. D. Beer, *Acc. Chem. Res.*, 1998, **31**, 71; P. D. Beer, P. A. Gale and G. Z. Chen, *J. Chem. Soc., Dalton Trans.*, 1999, 1897.
13 Problems associated with microanalysis of calixarenes have been previously reported: V. Bohmer, K. Jung, M. Schon and A. Wolff, *J. Org. Chem.*, 1992, **57**, 790; C. D. Gutsche and K. A. See, *J. Org. Chem.*, 1992, **57**, 4527.