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Anion binding by calix[4]arene ferrocene ureas

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A ferrocene reporting unit has been successfully incorporated onto the upper-rim of calix[4]arenes through either urea or amide hydrogen bonding units for the preparation of three novel receptors which can sense the binding of anions electrochemically. ^{1}H NMR studies indicate that the receptors have a general preference for binding more basic anions, and in the case of the tetra-urea derivative, a marked selectivity for dihydrogen phosphate. A single crystal X-ray structure of the di-urea derivative reveals the role of hydrogen bonding interactions in the binding of benzoate. Cyclic and square wave voltammetric studies demonstrate that all receptors can electrochemically sense the binding of anions with dihydrogen phosphate inducing the largest shifts.

Introduction

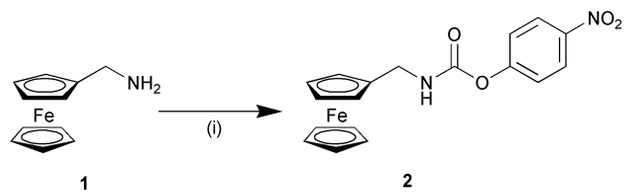
Anions play a number of crucial biological and environmental roles and their selective binding and sensing is an area of considerable current interest.[1] A variety of approaches to the binding of anions have been investigated since the early work of Simmons and Park on polyammonium cryptands,[2] with particular interest being focused on neutral receptors invoking hydrogen bond interactions (for example, amides and ureas). The importance of spatial pre-organisation of the complexing groups has been recognised and calixarenes in particular have been developed as scaffolds for the preparation of selective receptors.[3] In recent years both charged[4] and neutral[5] calix[4]arene based receptors have been prepared which show a high degree of tunability for selective anion complexation. We are particularly interested in combining hydrogen bonding interactions with sensing moieties to enable detection of anion binding *via* optical and electrochemical methods and to this end have prepared a number of such calixarene based receptors incorporating transition metal complexes of 2,2′-bipyridyl,[6] ferrocene[7] or cobaltocenium[8] as sensors. In this paper we describe the synthesis of two new calix[4]arene based receptors incorporating ferrocene urea moieties and contrast their anion complexation behaviour with that of a tetra-amidoferrocene calix[4]arene derivative using a combination of ^{1}H NMR spectroscopy and voltammetry.

Results and discussion

Synthesis

A variety of approaches to the preparation of calixarene ureas have been investigated, the majority based on the use of commercially available isocyanates[9] or isocyanate derivatives of calixarenes.[10] In this study the introduction of ferrocene ureas onto the calixarene skeleton has been achieved through reaction with an isocyanate synthon.[11] This method allows the isolation and purification of a less toxic reagent, enables a convergent approach based on amino functionalised calixarenes to the synthesis of both amide and urea derivatives, and is readily adaptable to the introduction of other more complex urea substituents.

Ferrocenemethylamine **1** was prepared following literature procedures[12] and converted to the nitrophenyl carbamate **2** (52% yield after chromatography) through reaction with *p*-nitrophenyl chloroformate (Scheme 1). This synthon reacted



1 **2**

Scheme 1 *Reagents and conditions*: (i) *p*-nitrophenol chloroformate, ethyldiisopropylamine, CH_2Cl_2.

readily with the tetra-amino **3**[13] and 1,3-di-amino **4**[10a] derivatives of tetrapropylcalix[4]arene (Schemes 2 and 3) in the presence of Hünig's base to yield the desired urea receptors **5** and **6** in 48 and 68% yields, respectively.

The tetra-amidoferrocene derivative **7** was prepared in excellent yield (90%) through treatment of **3** with chlorocarbonyl ferrocene[14] in the presence of triethylamine base (Scheme 2).

X-ray crystal structure of 7

X-ray quality single crystals of receptor **7** were grown by slow evaporation from chloroform–methanol. As Fig. 1 illustrates, the calixarene core adopts a flattened cone conformation in which opposed phenyl rings have parallel (interplanar angle 0.6°) or sharply inclined (interplanar angle 100.7°) positions. Associated with each receptor are three methanol molecules, the hydroxyl groups of which are hydrogen-bonded to the carbonyl oxygen atoms of the inclined fragments of the tetramer. Two of these occupy sites within the 'cusps' between the inclined and parallel fragments (O(9)–O(1) = 2.781(3) Å, O(10)–O(3) = 2.764(3) Å). A further hydrogen bond is formed by the interaction of the NH group of one of the adjacent parallel fragments with the oxygen atom of each (N(4)–O(9) = 2.912(4) Å, N(2)–O(10) = 2.888(4) Å). The remaining methanol molecule (not shown in Fig. 1) lies alongside the receptor, to which it is linked by a single hydrogen bond (O(11)–O(1) = 2.833(6) Å). In addition, the NH groups of the inclined fragments form intermolecular hydrogen bonds to carbonyl oxygen atoms of parallel fragments of adjacent tetramers (N(1)–O(3′) = 2.779(4) Å, N(3)–O(7″) = 2.775(4) Å).

Solution behaviour of 5

The solution behaviour of potential calixarene based anion receptors is important when considering their binding interactions with anions. The existence of inter- and intra-molecular

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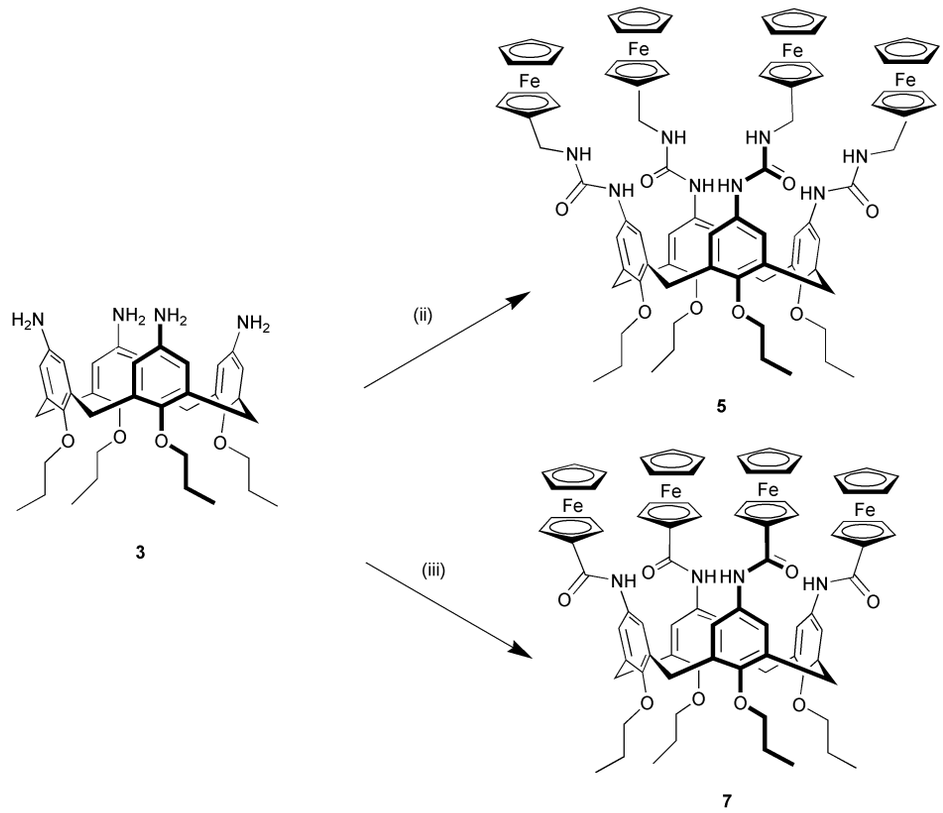
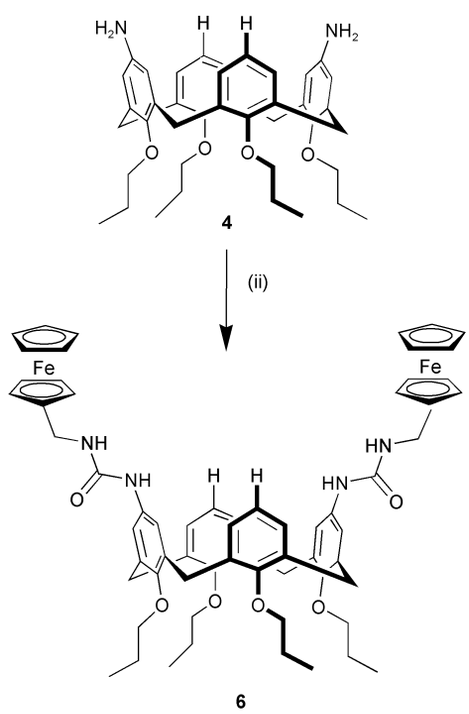


Scheme 2 *Reagents and conditions*: (ii) **2**, ethyldiisopropylamine, DMAP, CH_2Cl_2, (iii) chlorocarbonyl ferrocene, triethylamine, CH_2Cl_2.



Scheme 3 *Reagents and conditions*: (ii) **2**, ethyldiisopropylamine, DMAP, CH_2Cl_2.

hydrogen bonding interactions which must first be broken down before an anion binding event can take place are of particular relevance to calix[4]arene ureas. As has been previously noted for other derivatives,[9] the tetra-urea receptor **5** forms stable, solvent containing hydrogen-bonded dimers in non-polar solvents. The ^{1}H NMR spectrum of receptor **5** in C_6D_6 is shown in Fig. 2a. Two peaks are observed for the aromatic protons at 6.69 ppm (H_D) and 8.18 ppm (H_C), both are doublets with a typical meta-coupling of 2.5 Hz. In addition, the strong hydrogen bonds in the dimer cause deshielding of the urea protons resulting in the peaks for H_A and H_B appearing well downfield at 7.46 and 8.04 ppm, respectively. These dimers are kinetically labile and the rate of association/dissociation (6 s^{-1} at 60 °C for **5**·C_6D_6) determined by ^{1}H EXSY NMR experiments[15] is in agreement with previously reported values.[16] In contrast, with more competitive solvents such as d_6-DMSO (Fig. 2b) there is disruption of the dimeric structures through competition for the urea hydrogen bonds and a monomer spectrum is observed featuring a single signal for the aromatic protons (H_C and H_D). The spectral simplification from dimer to monomer is also observed on the addition of anions to chloroform solutions of receptor **5** which may be attributed to disruption of the hydrogen bonding array by the anion binding processes.

In contrast, both the 1,3-di-urea **6** and tetraamide **7** derivatives show no evidence of hydrogen bonding or association behaviour in solution, both adopting rapidly interconverting flattened cone conformations.

^{1}H NMR anion binding studies

The solution-phase anion co-ordination behaviour of receptors **5**, **6** and **7** was investigated by ^{1}H NMR titrations in a competitive solvent mixture of acetonitrile and DMSO (1 : 1). The anions chosen for these studies (chloride, benzoate and dihydrogen phosphate, added as their tetrabutylammonium salts) are of contrasting geometries and charge densities.

Addition of anions to the receptors resulted in significant downfield perturbations (of up to 2.32 ppm for **6** with benzoate) of the urea or amide protons indicating that the anions are bound by the hydrogen bonding moieties. Additional evidence for the binding of the anions in the vicinity of the upper-rim was provided by the downfield shifts of the signals for the aromatic protons *ortho* to the point of substitution.

Stepwise addition of anions to the receptors enabled the determination of association constants, as a measure of binding strength, from EQNMR[17] analysis of the titration curves (Table 1). Importantly, Job plots[18] revealed that the anion : receptor binding stoichiometry was 1 : 1 in all cases (for example, Fig. 3).

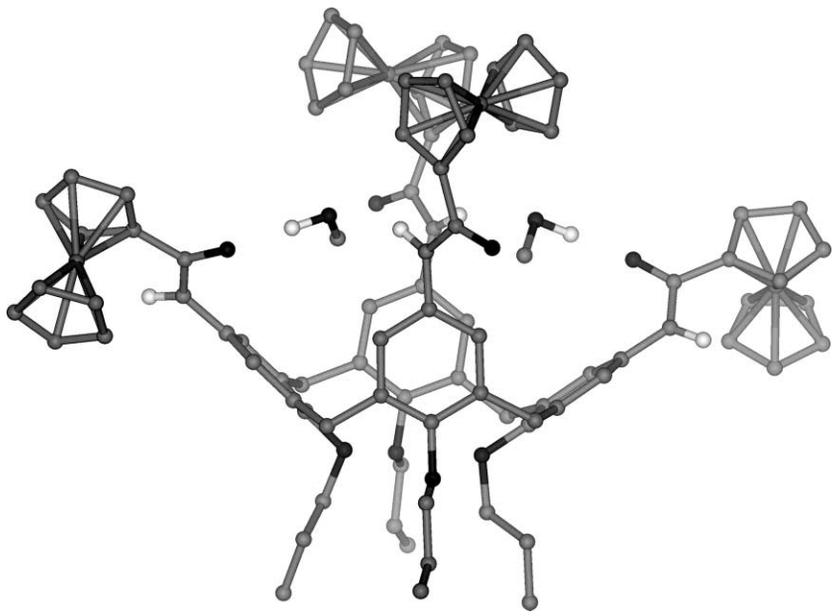


Fig. 1 General structural view of **7** showing the inclusion of two MeOH molecules (most of the hydrogen atoms have been omitted for clarity).

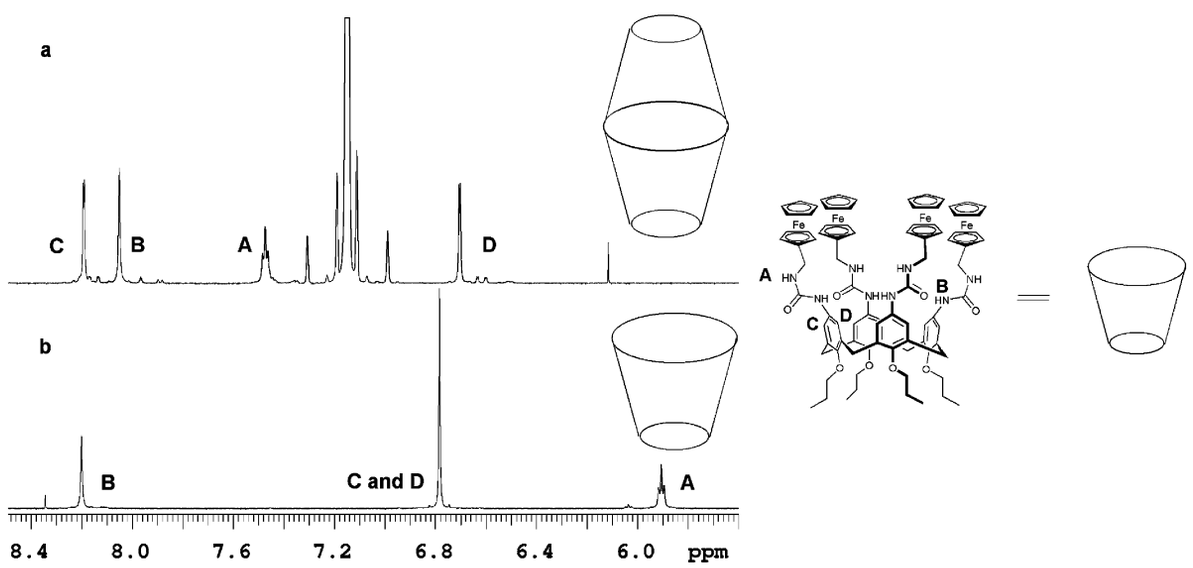


Fig. 2 Aromatic region of the ^{1}H NMR spectrum of receptor **5** in (a) C_6D_6 and (b) d_6-DMSO.

Table 1 Stability constant data for receptors **5**, **6** and **7** in 1 : 1 CD_3CN : d_6-DMSO

	K^a/dm^3 mol^{-1}		
Anion	**5**	**6**	**7**
Cl^-	15	15	30
$PhCO_2^-$	30	40	150
$H_2PO_4^-$	150	25	120

[a] Determined at 298 K; errors estimated to be ≤ 5%.

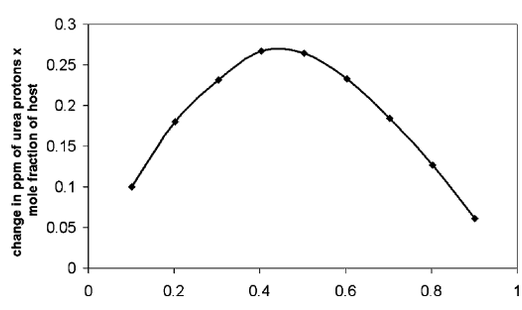


Fig. 3 Job plot for **6** and benzoate in 1 : 1 CD_3CN : d_6-DMSO revealing a 1 : 1 anion : receptor binding stoichiometry.

It is evident that the degree of upper-rim substitution has a marked effect on the binding properties of the receptors. The di-substituted receptor **6** exhibits modest association constants for all tested anions thus showing limited topological discrimination. This behaviour may be a consequence of the flexibility of the receptor which allows the binding cavity to distort sufficiently to accommodate the anion whilst retaining the maximum binding interactions. In contrast, the tetra-urea **5** and tetra-amide **7** receptors, in which the binding cavity is more defined and additional hydrogen bond donor sites are available, show significantly larger association constants, in particular for the more basic dihydrogen phosphate anion. Interestingly, the introduction of ureas does not result in markedly larger association constants compared to the amide receptor despite the higher acidity and increased anion binding ability of the urea NH protons.

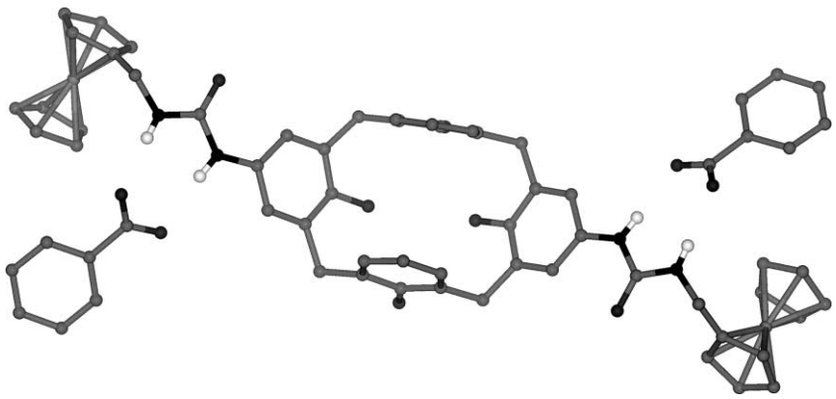


Fig. 4 General structural view of **6**·2[$N(C_4H_9)_4$][$PhCO_2$] (the propyl groups and most of the hydrogen atoms have been omitted for clarity).

Table 2 Electrochemical data for receptors **5**, **6** and **7**[a]

Receptor	E_{pa}[b]	E_{pc}	ΔE	I_{pa}/I_{pc}
5	82	−14	96	1.05
6	83	−2	85	1.05
7	265	165	100	1.10

[a] Conditions: 5×10^{-4} M solutions of receptors in 0.1 M NBu_4BF_4 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}. [b] relative to the $Ag/AgNO_3$ reference, errors ± 5 mV. $E_{½}$ ferrocene = 55 ± 5 mV *vs.* $Ag/AgNO_3$ reference electrode.

Table 3 Electrochemical anion recognition data for receptors **5**, **6** and **7**[a]

Anion	ΔE_{pa}/mV[b]		
	5	**6**	**7**
Cl^-	40	40	50
$PhCO_2^-$	50	70	20
$H_2PO_4^-$	220	180	200

[a] Conditions: 5×10^{-4} M solutions of receptors in 0.1 M NBu_4BF_4 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 mVs^{-1}. SWVs recorded with a scan increment of 2 mV and a frequency of 25 Hz. [b] Cathodic shift of oxidation potential produced by the prescence of 5 equivalents of anion added as the tetrabutylammonium salt. Errors ± 10 mV.

X-ray crystal structure of 6

Single crystals of **6**·2[$N(C_4H_9)_4$][$PhCO_2$] were obtained from a 1 : 1 acetonitrile : DMSO solution of the compound containing excess tetrabutylammonium benzoate. In contrast to the solution studies (Fig. 3), in the solid state the ferrocene urea groups act independently, binding benzoate in a 2 : 1 anion : receptor stoichiometry (Fig. 4). The calixarene molecule is situated on a crystallographic twofold axis of rotation and adopts a flattened cone conformation in which the two aromatic units substituted with ureas are flattened (the interplanar angle between the best planes of the attached phenyl groups is 113.2°). The other two phenyl groups taper inward slightly (interplanar angle 17.1°), effectively preventing the formation of any 'pocket'. Each urea is hydrogen-bonded through both NH groups to a benzoate anion (N(1)–O(4) = 2.949(2) Å, N(2)–O(5) = 2.813(2) Å), the urea and carboxylate groups not being coplanar (the interplanar angle between the NCN and OCO planes is 36.3°).

Electrochemical anion sensing studies

In order to evaluate the potential electrochemical sensor capabilities of receptors **5**, **6** and **7**, their voltammetric behaviour in the presence and absence of anions was investigated. Cyclic and square wave voltammograms were recorded for the receptors in a 1 : 1 CH_2Cl_2 : CH_3CN solvent mixture using NBu_4BF_4 as the supporting electrolyte. All receptors display a single quasi-reversible oxidation for the ferrocene/ferrocenium redox couple indicating that the ferrocene moieties act independently and are all oxidised at the same potential (Table 2).

On progressive addition of stoichiometric equivalents of anionic guest solutions, significant cathodic perturbations of the ferrocenes' oxidation potentials E_{pa} were observed for all receptors (Table 3), concomitant with the disappearance of the reduction wave E_{pc}. As reported previously with simple acyclic amide substituted ferrocene derivatives,[19] these cathodic shifts can be attributed to the binding of an anionic guest by the NH protons of the urea and amide groups in close proximity to the ferrocene redox centres, facilitating oxidation to ferrocenium. The disappearance of the reduction wave on anion addition indicates either that the complexed anion–ferrrocenium cation interaction is disfavouring reduction back to ferrocene or that an EC mechanism is in operation.

It is noteworthy that in all cases on addition of dihydrogen phosphate the appearance of a new E_{pa} wave is seen which increases to the detriment of the original wave (Fig. 5), whereas a single shifting wave is observed with chloride and benzoate (Fig. 6). This redox responsive behaviour with dihydrogen phosphate suggests the binding of this anion is kinetically slow on the CV or SWV timescale. Interestingly, for all receptors the largest magnitude of cathodic shift was noted with dihydrogen phosphate by up to ΔE_{pa} = 220 mV with **5**.

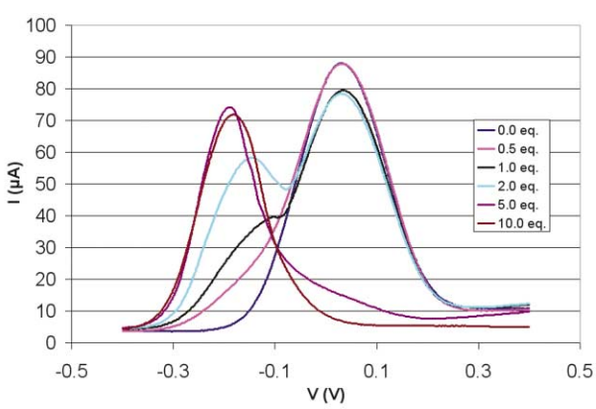


Fig. 5 Square wave voltammogram of **5** in the absence and presence of dihydrogen phosphate in 1 : 1 CH_2Cl_2 : CH_3CN.

Conclusion

New calixarene based anion receptors featuring di- or tetra-urea binding sites and ferrocene reporter units have been readily prepared, in acceptable yield, from a novel isocyanate synthon. ^{1}H NMR solution binding studies reveal these receptors and an

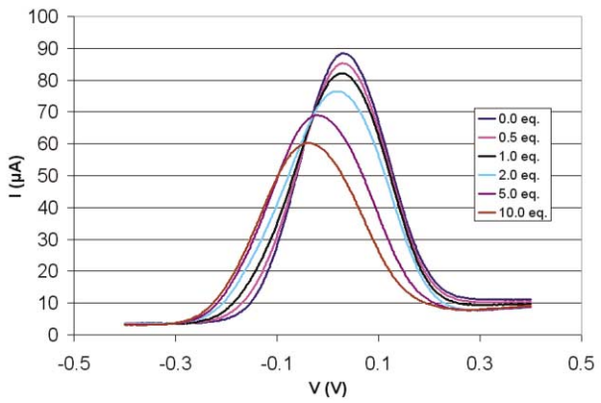


Fig. 6 Square wave voltammogram of **5** in the absence and presence of benzoate in 1 : 1 CH_2Cl_2 : CH_3CN.

analogous amide derivative bind anions in a 1 : 1 stoichiometry. Whilst the di-urea receptor **6** binds anions weakly and non-discriminatorily, both the tetra-urea **5** and tetra-amide **7** receptors generally show stronger binding and selectivity for more basic anions. X-ray crystallographic studies of **6** with benzoate confirm the involvement of hydrogen bonding interactions from the urea moieties in anion binding. All receptors show potential as electrochemical sensors for anions, with dihydrogen phosphate displaying markedly larger cathodic shifts than chloride and benzoate.

Experimental

General

All chemicals were commercial grade and used without further purification unless otherwise stated. Solvents were pre-dried and purified by distillation and stored under nitrogen where appropriate; dichloromethane and acetonitrile were dried by distillation over calcium hydride; triethylamine was distilled from potassium hydroxide. Tetrabutylammonium salts of chloride, benzoate and dihydrogen phosphate were stored in a dessicator under vacuum containing self-indicating silica. Ferrocenemethylamine **1**,[12] tetra-aminocalix[4]arene derivative **3**,[13] 1,3-di-aminocalix[4]arene derivative **4** [10a] and chlorocarbonyl ferrocene[14] were prepared according to literature procedures.

Nuclear magnetic resonance spectra were recorded using either a 300 MHz Varian VXWorks spectrometer or a 500 MHz Varian Unity spectrometer. Electrospray mass spectra were recorded using Micromass LCT equipment and microanalyses were obtained from an elementar vario EL.

Syntheses

Ferrocene mononitrophenolate 2. *p*-Nitrophenol chloroformate (432 mg, 2.14 mmol) and ethyldiisopropylamine (1 ml, excess) were added to a solution of ferrocenemethylamine (460 mg, 2.14 mmol) in CH_2Cl_2 (15 ml) and the resulting mixture stirred for 24 h. After evaporation of the solvent, the residue was purified by column chromatography (ethylacetate : hexane 4 : 1) to yield the desired product as an orange solid (420 mg, 52%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.23 (d, J = 9 Hz, ONp, 2H), 7.28 (d, J = 9 Hz, ONp, 2H), 5.25 (br t, N*H*, 1H), 4.23 (s, FeCp, 2H), 4.21 (s, CH_2NH & FeCp, 9H). FAB MS *m*/*z*: 380 (M), 403 (M + Na).

Tetra-ferrocene-urea functionalised calix[4]arene receptor 5. Tetra-aminocalix[4]arene derivative **3** (500 mg, 0.77 mmol) in CH_2Cl_2 (20 ml) was added dropwise to a stirred solution of **2** (1750 mg, 4.61 mmol), ethyldiisopropylamine (2 ml, excess) and DMAP (catalytic) in CH_2Cl_2 (20 ml) and the mixture was stirred for 24 h under nitrogen. The reaction mixture was washed repeatedly with sodium carbonate solution (10%, 4 × 50 mL) then the organic fraction was dried over anhydrous magnesium sulfate, filtered, and the solvent removed under vacuum. The residue was purified by column chromatography (silica, $CHCl_3$: MeOH 10 : 1). The product was obtained as a pale yellow powder after precipitation from a $CHCl_3$–hexane solution (590 mg, 48%). ^{1}H NMR (500 MHz, d_6-DMSO): δ 8.19 (s, ArN*H*, 4H), 6.77 (s, Ar*H*, 8H), 5.90 (t, J = 5.5 Hz, CH_2N*H*, 4H), 4.30 (d, J = 13.0 Hz, ArCH_{ax}Ar, 4H), 4.16 (s, C_5H_5, 20H), 4.13 (s, C_5H_4, 8H), 4.07 (s, C_5H_4, 8H), 3.93 (d, J = 5.5 Hz, CH_2NH, 8H), 3.74 (t, J = 7.5 Hz, OCH_2CH$_2$CH$_3$, 8H), 3.02 (d, J = 13.0 Hz, ArCH_{eq}Ar, 4H), 1.89 (sext, J = 7.5 Hz, OCH$_2$-CH_2CH$_3$, 8H), 0.93 (t, J = 7.5 Hz, OCH$_2$CH$_2$CH_3, 12H). ^{1}H NMR (500 MHz, C_6D_6): δ 8.18 (d, J = 2.5 Hz, Ar*H*, 4H), 8.04 (s, ArN*H*, 4H), 7.46 (t, J = 5.5 Hz, CH_2N*H*, 4H), 6.69 (d, J = 2.5 Hz, Ar*H*, 4H), 4.76 (d, J = 12.0 Hz, ArCH_{ax}Ar, 4H), 4.51 (dd, J = 14.5 & 5.5 Hz, CH_2NH, 4H), 4.45 (dd, J = 14.5 & 5.5 Hz, CH_2NH, 4H), 4.41 (s, C_5H_4, 4H), 4.22 (s, C_5H_4, 4H), 4.11 (s, C_5H_5, 20H), 3.93 (s, C_5H_4, 4H), 3.89 (t, J = 7.5 Hz, OCH_2-CH$_2$CH$_3$, 8H), 3.85 (s, C_5H_4, 4H), 3.43 (d, J = 12.0 Hz, ArCH_{eq}Ar, 4H), 2.07 (sext, J = 7.5 Hz, OCH$_2$CH_2CH$_3$, 8H), 0.89 (t, J = 7.5 Hz, OCH$_2$CH$_2$CH_3, 12H). ES-MS *m*/*z*: 1617.5 (M + H$^+$), 1656.4 (M + K$^+$). Elemental analysis, found: C, 63.5; H, 5.8; N, 6.8%. $C_{88}H_{96}Fe_4N_8O_8$·½$CHCl_3$ requires C, 63.4; H, 5.8; N, 6.7%.

1,3-Di-ferrocene-urea functionalised calix[4]arene receptor 6. **2** (400 mg, 1.06 mmol), ethyldiisopropylamine (1 ml, excess) and DMAP (catalytic) were added to a solution of 1,3-diaminocalix[4]arene derivative **4** (300 mg, 0.48 mmol) in CH_2Cl_2 (10 ml). The solution was stirred for 18 h and monitored by TLC. The mixture was washed repeatedly with 10% Na_2CO_3, dried and the solvent evaporated. The residue was purified by column chromatography (CH_2Cl_2 : MeOH 9 : 1) to yield the product as a pale orange foam (360 mg, 68%). ^{1}H NMR (500 MHz, d_6-DMSO): δ 8.23 (s, ArN*H*, 2H), 6.96 (s, Ar*H*, 4H), 6.41 (m, Ar*H*, 6H), 6.02 (t, J = 5.5 Hz, CH_2N*H*, 2H), 4.30 (d, J = 13.0 Hz, ArCH_{ax}Ar, 4H), 4.17 (m, C_5H_4 & C_5H_5, 14H), 4.09 (s, C_5H_4, 4H), 3.97 (d, J = 5.5 Hz, CH_2NH, 4H), 3.80 (t, J = 7.5 Hz, OCH_2CH$_2$CH$_3$, 4H), 3.68 (t, J = 7.5 Hz, OCH_2-CH$_2$CH$_3$, 4H), 3.06 (d, J = 13.0 Hz, ArCH_{eq}Ar, 4H), 1.88 (sext, J = 7.5 Hz, OCH$_2$CH_2CH$_3$, 4H), 1.84 (sext, J = 7.5 Hz, OCH$_2$-CH_2CH$_3$, 4H), 0.99 (t, J = 7.5 Hz, OCH$_2$CH$_2$CH_3, 6H), 0.88 (t, J = 7.5 Hz, OCH$_2$CH$_2$CH_3, 6H). ^{1}H NMR (300 MHz, C_6D_6): δ 7.10 (d, J = 7.5 Hz, Ar*H*, 4H), 6.95 (t, J = 7.5 Hz, Ar*H*, 2H), 6.70 (s, ArN*H*, 2H), 6.34 (s, Ar*H*, 4H), 5.47 (t, CH_2N*H*, 2H), 4.47 (d, J = 13.5 Hz, ArCH_{ax}Ar, 4H), 4.16 (d, J = 5.0 Hz, CH_2NH, 4H), 4.13 (s, C_5H_4, 4H), 4.00 (s, C_5H_5, 10H), 3.93 (s, C_5H_4, 4H), 4.00 & 3.55 (both t, J = 7.5 Hz, OCH_2CH$_2$CH$_3$, 2 × 4H), 3.09 (d, J = 13.5 Hz, ArCH_{eq}Ar, 4H), 1.90 (sext, J = 7.5 Hz, OCH$_2$CH_2CH$_3$, 4H), 1.66 (sext, J = 7.5 Hz, OCH$_2$-CH_2CH$_3$, 4H), 0.91 (t, J = 7.5 Hz, OCH$_2$CH$_2$CH_3, 6H), 0.77 (t, J = 7.5 Hz, OCH$_2$CH$_2$CH_3, 6H). ES-MS *m*/*z*: 1105.6 (M + H$^+$). Elemental analysis, found: C, 68.7; H, 6.4; N, 4.7%. $C_{64}H_{72}$-$Fe_2N_4O_6$ requires C, 69.6; H, 6.6; N, 5.1%.

Tetra-ferrocene-amide functionalised calix[4]arene receptor 7. Tetra-aminocalix[4]arene derivative **3** (500 mg, 0.77 mmol) in CH_2Cl_2 (50 ml) was added dropwise to a stirred solution of chlorocarbonyl ferrocene (1150 mg, 4.63 mmol) and triethylamine (5 ml, excess) in CH_2Cl_2 (50 ml) and the mixture was stirred for 48 h under nitrogen. Water (100 ml) was added and the mixture stirred for 30 min. 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 yellow/orange powder after precipitation from a $CHCl_3$–hexane solution, followed by filtration and washing with hexane (1040 mg, 90%). ^{1}H NMR (300 MHz, d_6-DMSO): δ 9.18 (s, N*H*, 4H), 7.18 (s, Ar*H*, 8H), 4.86 (s, C_5H_4, 8H), 4.43 (d, J = 12.6 Hz, ArCH_{ax}Ar, 4H), 4.31 (s,

C_5H_4, 8H), 4.14 (s, C_5H_5, 20H), 3.85 (t, J = 7.5 Hz, OCH_2-CH_2CH_3, 8H), 3.20 (d, J = 12.6 Hz, $ArCH_{eq}Ar$, 4H), 1.98 (sext, J = 7.5 Hz, $OCH_2CH_2CH_3$, 8H), 1.00 (t, J = 7.5 Hz, OCH_2-CH_2CH_3, 12H). FAB-MS m/z: 1501.5 (M), 1524.5 (M + Na). Elemental analysis, found: C, 66.5; H, 5.1; N, 3.7%. $C_{84}H_{84}$-$Fe_4N_4O_8$ requires C, 67.2; H, 5.6; N, 3.7%.

X-ray crystallography

Typically a single crystal was mounted on a glass fibre using perfluoropolyether oil and cooled rapidly to 150K in a stream of cold N_2 using an Oxford Cryosystems CRYOSTREAM unit. Diffraction data were measured using an Enraf-Nonius Kappa CCD diffractometer (graphite-monochromated Mo Kα radiation, λ = 0.71073 Å). Intensity data were processed using the DENZO-SMN package.[20] The structure was solved using the direct-methods program SIR92,[21] which located all non-hydrogen atoms. Subsequent full-matrix least-squares refinement was carried out using the CRYSTALS program suite.[22] Coordinates and anisotropic thermal parameters of all non-hydrogen atoms were refined. All hydrogen atoms were positioned geometrically after each cycle of refinement. A four-term Chebychev polynomial weighting scheme was applied.

CCDC reference numbers 216792 and 216793.

See http://www.rsc.org/suppdata/dt/b3/b309288g/ for crystallographic data in CIF or other electronic format.

Crystal data for 7·3MeOH·3CHCl$_3$. Crystals were grown by slow evaporation from chloroform–methanol. $C_{90}H_{98}Cl_9Fe_4$-N_4O_{11}, M = 1954.26, triclinic, a = 14.1072(1), b = 17.9519(1), c = 20.8413(2) Å, α = 70.9519(4), β = 82.2956(4), γ = 68.8153(4)°, U = 4533.4 Å^3, T = 150 K, space group $P\bar{1}$, Z = 2, μ(Mo Kα) = 0.953 mm^{-1}, 85895 reflections measured, 20463 unique (R_{int} = 0.047) which were used in all calculations. The final wR (F^2) was 0.0704 (all data).

Crystal data for 6·2[N(C$_4$H$_9$)$_4$][PhCO$_2$]. Crystals were grown from a 1 : 1 acetonitrile : DMSO solution containing excess tetrabutylammonium benzoate. $C_{110}H_{154}Fe_2N_6O_{10}$, M = 1832.16, monoclinic, a = 20.7844(4), b = 9.1206(3), c = 53.0777(15) Å, β = 95.1009(8)°, U = 10021.9 Å^3, T = 150 K, space group C 2/c, Z = 4, μ(Mo Kα) = 0.351 mm^{-1}, 45147 reflections measured, 11837 unique (R_{int} = 0.061) which were used in all calculations. The final wR (F^2) was 0.0472 (all data).

^{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[15] to yield stability constants for the anion/receptor binding processes.

Electrochemistry

Cyclic voltammetry (CV) and square wave voltammetry (SWV) experiments 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 ($E_{½}$ ferrocene = 55 ± 5 mV *vs.* 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 a 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.

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