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Ion-pair recognition by a ditopic calix[4]semitube receptor

Philip R. A. Webber and Paul D. Beer *
Department of Chemistry, Inorganic Chemistry Laboratory, University of Oxford, South Parks Road, Oxford, UK OX1 3QR

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A ditopic receptor comprised of a calix[4]semitube for cation recognition and urea functionality for anion complexation has been developed. This receptor displays a remarkable selectivity and fast kinetics of complexation for potassium cation over all other Group 1 metal cations, a property mirroring that of the parent calix[4]semitube **1**. ^{1}H NMR studies reveal that **4** cooperatively binds a range of sodium and potassium halide and acetate salts in 2 : 1 $CDCl_3$: CD_3CN, with anion binding enhancements of over thirty-fold in the case of bromide. Extraction experiments demonstrated that the host could solubilise sodium and potassium salts in chloroform.

Introduction

The simultaneous binding of cationic and anionic guest species by heteroditopic receptors is a rapidly developing new field of coordination chemistry.[1] Such systems have potential as new selective extraction and transportation reagents for metal salt ion-pair species of environmental importance.[2] In addition, ion-pair receptors can be used to mimic important biological functions[3] and coordinate biologically significant species such as zwitterionic amino acids and peptides.[4]

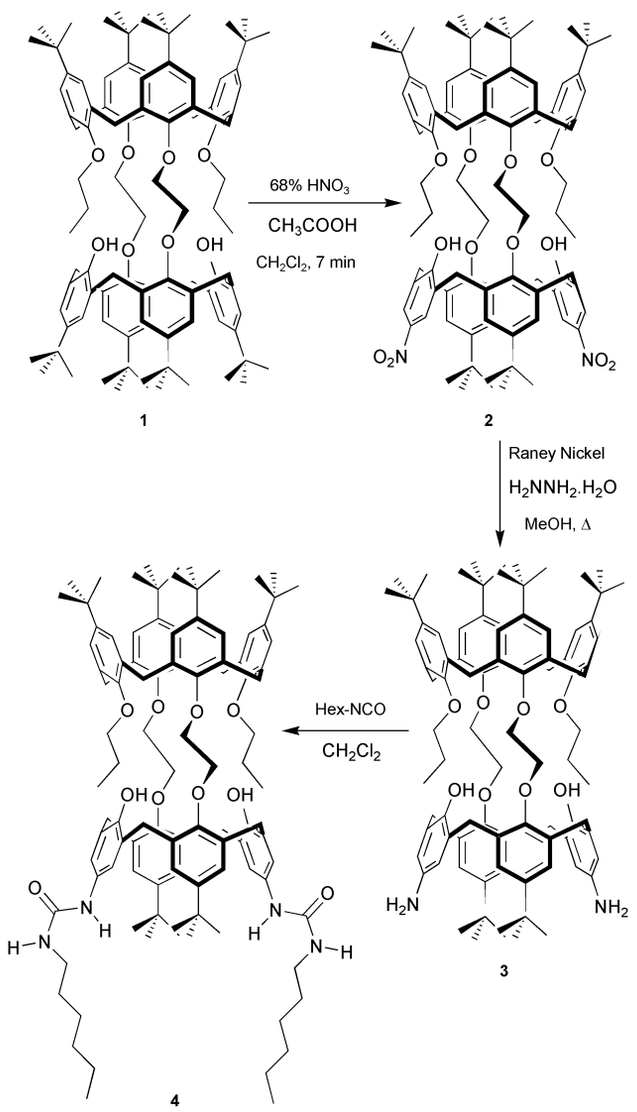
Ion-pair receptors to date have been based on hydrogen bonding, positively charged or Lewis acidic groups to coordinate the anion, and crown ether or modified calixarenes to bind the cation.[1–5] These ditopic host molecules often exhibit cooperative and allosteric effects whereby the association of one ion influences the binding affinity of the counter ion.[5] The cooperativity can be positive or negative, depending on whether the binding affinity is enhanced or reduced, respectively. Cooperative behaviour can result from several factors, such as through-space or through-bond electrostatic interactions between bound ion-pairs or conformational changes induced by binding. We report here the synthesis of a novel ditopic calix[4]semitube receptor which exhibits a remarkable selectivity for potassium cations, and, cooperatively binds a range of sodium and potassium halide and acetate salts.

Results and discussion

We recently reported a new class of ionophore, the calix[4]-semitube **1**, consisting of two calix[4]arene units linked by two ethylene chains at the lower rim, together with propyl ether groups which exhibits remarkable selectivity for potassium over all Group 1 metal cations.[6] With the aim of producing a heteroditopic receptor specifically for potassium salts the synthesis of a calix[4]semitube modified with additional urea hydrogen bonding recognition sites for anions was undertaken.

Synthesis

Nitration of calix[4]semitube **1** using 68% nitric acid and glacial acetic acid afforded the dinitro product **2** in 19% yield. Reduction of **2** with Raney nickel and hydrazine monohydrate in refluxing methanol gave the diamine **3** in 85% yield. Condensation of **3** with an excess amount of hexyl isocyanate in dichloromethane produced the target ditopic calix[4]semitube receptor **4** in 62% yield (Scheme 1). The receptor was characterised by ^{1}H NMR spectroscopy, electrospray mass spectrometry and elemental analysis (see Experimental section).



Scheme 1 Synthesis of the heteroditopic receptor.

^{1}H NMR binding studies

Group 1 metal cation complexation. Preliminary experiments were undertaken on the ditopic calix[4]semitube **4** to establish the receptor's kinetic complexation behaviour towards Na^+, K^+ and Rb^+ cations. The addition of one equivalent of $NaClO_4$, KPF_6 or $RbPF_6$ to 5 : 1 $CDCl_3$: CD_3CN and 4 : 1 $CDCl_3$: CD_3OD solutions of **4** revealed that although the complexation/decomplexation process was slow on the NMR timescale,

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Table 1 Stability constant data[a] for the alkali metal complexes of **4**

	K/M^{-1}	
	5 : 1 $CDCl_3$: CD_3CN	4 : 1 $CDCl_3$: CD_3OD
Na^+	$>10^5$	30
K^+	$>10^5$	$>10^5$
Rb^+	2000	80
Cs^+	0	0

[a] At 291 K. The alkali metal cations were added as their perchlorate or hexafluorophosphate salts.

new resonances for the respective metal cation complex were observed, the time required for each complexation to reach equilibrium was fast (≤4 minutes to acquire the ^1H NMR spectrum). These cation complexation results are similar to those noted with the parent calix[4]semitube **1**[6] and contrast the slow kinetics of potassium cation complexation exhibited by calix[4]tubes.[7] Stability constants were determined by direct integrations of host and complex resonances in the ^1H NMR spectrum and the values are shown in Table 1.

Excellent selectivity for K^+ is displayed by **4** with stability constant values of similar magnitudes to those of the parent semitube **1**. This suggests urea upper rim functionalisation of the calix[4]semitube structure does not affect binding strength or the selectivity properties of this class of ionophore.

Fig. 1 displays the changes in the spectra of **4** upon addition of Na^+ and K^+ cations in 5 : 1 $CDCl_3$: CD_3CN. The aromatic region in free **4** shows that one calixarene unit is adopting a regular cone conformation and the other a pinched cone; it is expected that the calixarene moiety bearing the propyl groups adopts the pinched cone conformation as this is observed in the X-ray crystal structure of **1**. The other calixarene with attached urea moieties is likely to adopt the regular cone structure due to lower rim OH ··· OR hydrogen bonding. This means that the urea groups should be free for anion coordination unlike Reinhoudt and co-workers' upper rim urea derivatised tetraestercalix[4]arene where intramolecular hydrogen bonding between opposite urea moieties inhibited anion complexation in the free ligand.[5a] The urea NH protons appear at around 4.8 and 6.1 ppm and the OH protons at 9.2 ppm.

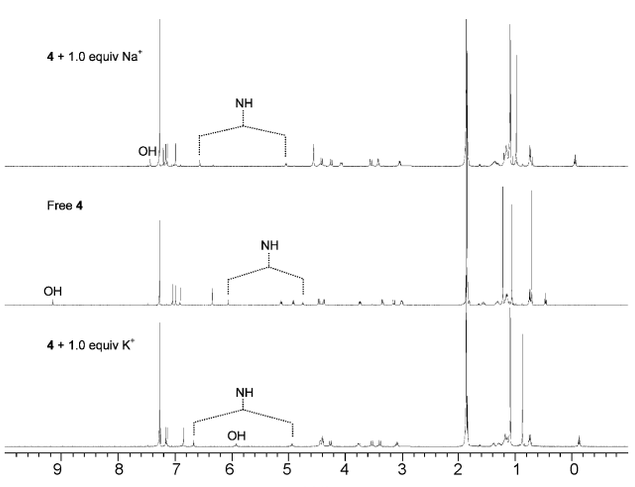

Fig. 1 The changes in the ^1H NMR spectrum of **4** upon addition of one equivalent of sodium and potassium cations in 5 : 1 $CDCl_3$: CD_3CN.

The ^1H NMR spectra of the Na^+ and K^+ complexes display some similarities. For instance, the chemical shift values of the aromatic resonances indicate that both adopt regular cone conformations of the calixarene units upon complexation. However, there are also some interesting differences, most notably the position of the OH resonance. In both cases, it has shifted upfield compared to the free ligand, however in the Na^+ complex it appears at 7.4 ppm but in the K^+ complex at 5.95 ppm. This implies that K^+ is a much better fit in the cavity than Na^+, withdrawing more electron density away from the OH oxygen despite being of lower polarising power. The most likely route of entry of K^+ is *via* a horizontal or 'side-on' route as noted from the results of molecular modelling simulations with **1**.

Table 2 Stability constant data[a] for the anion complexes of **4**, [**4**·Na^+] and [**4**·K^+] in 2 : 1 $CDCl_3$: CD_3CN

	K/M^{-1}		
	Free **4**	[**4**·Na^+][b]	[**4**·K^+][b]
Cl^-	60	[c]	>730[d]
Br^-	20	620	550
I^-	15	280	310
OAc^-	110	[c]	710

[a] At 291 K. Maximum error estimated to be ±10%. [b] Ligand to which one equivalent of cation has been added. Cations were added as their perchlorate or hexafluorophosphate salts. [c] Sodium salt of the given anion precipitated. [d] Ligand is only 89% cation complexed at the end of the titration (i.e. with 7 equiv. of anion).

Anion and ion-pair complexation. As discussed above, it was expected that the calixarene bearing the urea groups adopts a regular cone conformation, with no hydrogen bonding between the ureas. This was confirmed upon addition of anions to the free ligand as shifts were observed in the urea NH protons. Unlike cation complexation, anion binding produced continuous shifts in the proton resonances indicating fast exchange. Consequently, stability constants were determined using the computer program EQNMR.[8] Titration experiments were conducted on **4** with anions, added as their tetrabutylammonium salts, both in the presence and absence of one equivalent of Na^+ and K^+ cations. The choice of solvent for these experiments was limited because all possible species that might exist in the titration experiment (most importantly the ion-pair being studied, the receptor and the receptor ion-pair complex) 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 and finally, the stability constant for anion binding both with and without a cobound cation has to be less than 10^4 otherwise it could not be fitted accurately by EQNMR. The results for the titrations conducted in 2 : 1 $CDCl_3$: CD_3CN are displayed in Table 2. This solvent mixture satisfied the above criteria for the majority of the experiments performed.

Evidently, the free ligand **4** binds anions weakly with a selectivity of $Cl^- > Br^- > I^-$ amongst the halides. The bidentate acetate anion displays stronger binding than all of the halides tested, in part reflecting its greater basicity. When **4** is cation complexed, very significant anion binding enhancements are observed up to around thirty-fold for Br^-. There were some precipitation problems for the sodium bound receptor with the formation of NaCl and NaOAc quantitatively occurring; this could be ascertained by seeing the resonances for the Na^+ complex revert back to the resonances of the free ligand. This also partially occurred for the K^+ complex with chloride although only to the extent of 11% conversion back with 7 equivalents of anion. The quoted stability constant for this system is therefore somewhat understated. Surprisingly, only a small enhancement was observed for acetate with K^+, considerably less than that for bromide or iodide.

Table 2 shows that metal cation complexation can effectively be seen to 'switch on' anion binding of Br^- and I^- as the free ligand anion binding constants are very small and the enhancements particularly large. For all of the cases, an augmentation in stability constant can be ascribed to (i) an increase in acidity of the urea NH protons due to the electron

withdrawing effect of the bound cation; (ii) rigidification of the calixarene units through cation complexation and (iii) an electrostatic attraction between bound cation and anion (Fig. 2).

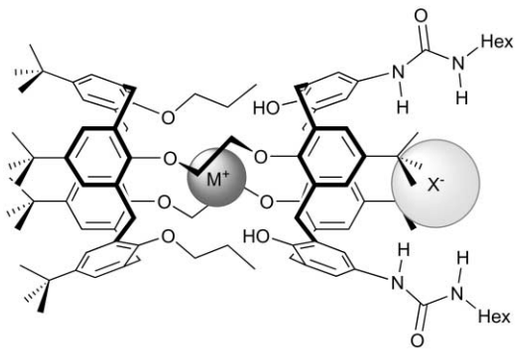

Fig. 2 Schematic representation of ditopic receptor **4** complexing an ion-pair.

Whereas the addition of anions to free **4** resulted in small downfield shifts of the NH resonances, the addition to metal cation complexed **4** gave much larger shifts as demonstrated in Fig. 3 for the titration of $\mathbf{4}\cdot K^+$ with iodide anions. A significant shift also occurred for the OH resonance of the receptor which moved upfield by 0.08 ppm (with 7 equivalents of anion) for the example given, presumably due to the electrostatic attraction between the iodide anion and bound cation causing the cation to interact more strongly with the oxygen of the OH group. There was also a small shift of one of the aromatic resonances, probably that of the protons *ortho* to the urea group; anion complexation will make the orientation of the ring to which they are attached alter.

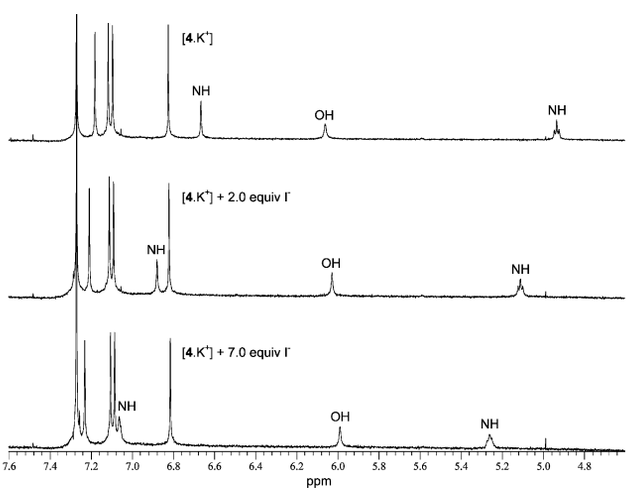

Fig. 3 The changes in the ^{1}H NMR spectrum of $[\mathbf{4}\cdot K^+]$ upon addition of iodide anions in 2 : 1 $CDCl_3$: CD_3CN.

Fig. 4 displays the binding curves for free **4** and $\mathbf{4}\cdot K^+$ with iodide anions. The increased steepness of the slope of the latter is indicative of a greater stability constant value.

Extraction studies

As mentioned in the introductory paragraph a potential application of neutral ion-pair receptors is the extraction and transport of metal salts. The extraction experiments performed assess the extent to which the ditopic receptor **4** could solubilise NaX and KX salts (X = Cl, Br, I, OAc) in chloroform. For each, to 1 mg of receptor and an excess of the solid sodium or potassium salt was added 600 μl of deuterated chloroform. The mixtures were then shaken mechanically for 48 hours and their proton NMR spectra taken after filtration. The relative amount of complex formed was determined on the basis of the integrations of the ^{1}H NMR signals for the aromatic hydrogens of the complex and free ligand.

Table 3 Extraction percentages of Group 1 halide and acetate salts by **4** into $CDCl_3$

	Complex (%) [lattice energy[a]/kJ mol^{-1}]	
	Na^+	K^+
Cl^-	0 [786]	0 [715]
Br^-	3 [747]	13 [682]
I^-	27 [704]	95 [649]
OAc^-	0 [763]	13 [682]

[a] Of the Group 1 metal cation salt.

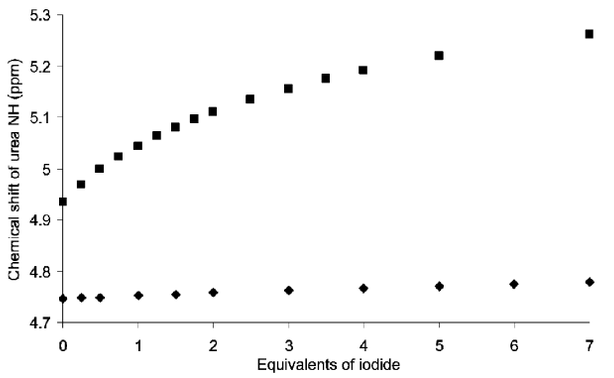

Fig. 4 ^{1}H NMR titration curves for one of the urea protons of **4** (◆) and $\mathbf{4}\cdot K^+$ (■) in 2 : 1 $CDCl_3$: CD_3CN.

Table 3 shows that the percentage complex formed approximately mirrors the lattice energy of the salt being solubilised. Most importantly, large shifts were observed in both the calixarene framework protons and the urea NH protons, consistent with both cation and anion having been complexed. It is perhaps surprising that the percentage complex for the potassium salts is not greater considering that K^+ is bound much more strongly than Na^+. Attempts to observe the neutral ion-pair complexes by FAB MS failed with only the cation-bound cluster being seen.

Conclusion

A new heteroditopic receptor consisting of an ethylene bridged calix[4]semitube moiety and two urea functionalities, positioned on the upper rim of one of the calix[4]arene units, has been synthesised in three steps from the parent calix[4]semitube **1**. Proton NMR investigations with alkali metal cations revealed that the host displayed a remarkable selectivity and fast kinetics of complexation for potassium cation over all other Group 1 metal cations with stability constant values similar to those of **1**. Whereas **4** only binds halide and acetate anions very weakly in 2 : 1 $CDCl_3$: CD_3CN, the sodium and potassium ion complexes of **4** form much more stable complexes with these anions, with anion binding enhancements of over thirty-fold in the case of bromide anion. It can therefore be stated that **4** cooperatively binds a range of sodium and potassium halide and acetate salts in 2 : 1 $CDCl_3$: CD_3CN with the bound Group 1 metal cation effectively 'switching on' anion complexation. Extraction experiments demonstrated that the host is capable of solubilising sodium and potassium salts in chloroform.

Experimental

General

All chemicals were commercial grade and used without further purification unless otherwise stated. Solvents were predried,

purified by distillation and stored under nitrogen where appropriate. Dichloromethane was distilled from calcium hydride.

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. Microanalyses were obtained on an elementar vario EL and were performed by the Inorganic Chemistry Laboratory, University of Oxford.[10]

tert-Butyl ethylsemitube **1** was prepared according to a previously described method.[6]

Syntheses

Dinitro *tert*-butyl ethylsemitube 2. To a rapidly stirred solution of *tert*-butyl ethylsemitube **1** (0.25 g, 0.17 mmol) in dichloromethane (4.5 ml) at room temperature was added a mixture of 68% nitric acid (0.54 ml, 5.3 mmol) and glacial acetic acid (0.54 ml). After 7 minutes (check by TLC), the reaction was quenched by addition of water (20 ml). The organic layer was separated, washed with water (20 ml), dried ($MgSO_4$) and reduced *in vacuo*. The residue was purified by column chromatography on silica gel eluting with 80 : 20 : 0.2 (v/v/v) chloroform : hexane : acetic acid over a 16 cm depth column under gravity. The desired product was second off the column and was isolated as a pale yellow powder (45 mg, 19%) (Found: C, 71.77; H, 7.84; N, 1.95%. $C_{90}H_{110}O_{12}N_2 \cdot CHCl_3$ requires C, 71.38; H, 7.31; N, 1.83%); δ_H(300 MHz, $CDCl_3$) 0.61 (6H, t, ^3J = 7.5 Hz, $OCH_2CH_2CH_3$), 0.80 (s, 18H, $(CH_3)_3C$), 1.21 (s, 18H, $(CH_3)_3C$)), 1.32 (s, 18H, $(CH_3)_3C$), 1.68 (m, 4H, $OCH_2CH_2CH_3$), 3.26 (4H, d, ^2J = 13.0 Hz, $ArCH_2Ar$), 3.58 (4H, d, ^2J = 13.0 Hz, $ArCH_2Ar$), 3.87 (4H, t, ^3J = 7.5 Hz, $OCH_2CH_2CH_3$), 4.52 (4H, d, ^2J = 13.0 Hz, $ArCH_2Ar$), 4.54 (4H, d, ^2J = 13.0 Hz, $ArCH_2Ar$), 5.08 (4H, t, ^3J = 8.0 Hz, $ROCH_2CH_2OR'$), 5.28 (4H, t, ^3J = 8.0 Hz, $ROCH_2CH_2OR'$), 6.42 (4H, s, Ar*H*), 7.15 (4H, s, Ar*H*), 7.19 (4H, s, Ar*H*), 8.00 (4H, s, Ar*H*), 10.63 (2H, s, OH); δ_C(75 MHz, $CDCl_3$) 10.28 ($OCH_2CH_2CH_3$), 22.95 ($OCH_2CH_2CH_3$), 31.12, 31.26 and 31.68 ($(CH_3)_3C$), 32.18, 33.11, 33.56, 34.07 and 34.33 ($(CH_3)_3C$ and $ArCH_2Ar$), 70.77, 74.37 and 77.66 (OCH_2), 124.28, 124.62, 125.88, 127.06, 129.23, 131.27, 131.45, 134.77, 140.46, 144.12, 145.12, 148.45, 149.95, 153.09, 154.26 and 159.26 (Ar); MS (ES): *m*/*z* 1450 ($M + K^+$).

Diamino *tert*-butyl ethylsemitube 3. To a stirred suspension of the dinitro derivative **2** (80 mg, 0.06 mmol) in methanol (25 ml) was added Raney nickel (washed with 2 × 5 ml portions of methanol) and hydrazine monohydrate (1.5 ml). The mixture was refluxed for 18 h and then hot-filtered over Celite. After washing the Celite with dichloromethane (25 ml), the organic solvents were removed *in vacuo* yielding pure **3** as a bright yellow powder (70 mg, 85%); δ_H(300 MHz, $CDCl_3$) 0.76 (6H, t, ^3J = 7.2 Hz, $OCH_2CH_2CH_3$), 0.83 (18H, s, $(CH_3)_3C$), 1.25 (18H, s, $(CH_3)_3C$)), 1.35 (18H, s, $(CH_3)_3C$), 1.74 (4H, m, $OCH_2CH_2CH_3$), 3.24 (4H, d, ^2J = 12.9 Hz, $ArCH_2Ar$), 3.30 (4H, d, ^2J = 12.3 Hz, $ArCH_2Ar$), 4.10 (4H, t, ^3J = 7.2 Hz, $OCH_2CH_2CH_3$), 4.59 (8H, d, ^2J = 12.9 Hz, 2 × [$ArCH_2Ar$]), 5.16 (4H, br t, $ROCH_2CH_2OR'$), 5.25 (br t, 4H, $ROCH_2CH_2OR'$), 6.31 (4H, s, Ar*H*), 6.41 (4H, s, Ar*H*), 7.05 (4H, s, Ar*H*), 7.11 (4H, s, Ar*H*), 8.45 (2H, s, O*H*); MS (ES): *m*/*z* 1353 ($M + H^+$), 1375 ($M + Na^+$), 1391 ($M + K^+$).

Di[hexylureido] *tert*-butyl ethylsemitube 4. To a stirred solution of the diamine **3** (70 mg, 0.05 mmol) in dichloromethane (20 ml) was added hexyl isocyanate (0.06 g, 0.5 mmol) and the mixture refluxed for 20 h. The solvent was removed *in vacuo* and hexane added to the residue. The yellow precipitate which formed was filtered and identified as pure **4** (50 mg, 62%) (Found: C, 70.49; H, 8.21; N, 3.62%. $C_{104}H_{140}O_{10}N_4 \cdot 7/3(CH_2Cl_2)$ requires C, 70.77; H, 8.08; N, 3.10%); δ_H(300 MHz, $CDCl_3$) 0.68 (6H, t, ^3J = 7.5 Hz, $OCH_2CH_2CH_3$), 0.84 (18H, s, $(CH_3)_3C$), 0.86 (6H, t, ^3J = 7.5 Hz, $NH(CH_2)_5CH_3$), 1.23 (18H, s, $(CH_3)_3C$), 1.25 (12H, m, $NH(CH_2)_2(CH_2)_3CH_3$), 1.31 (4H, m, $NHCH_2CH_2$), 1.36 (18H, s, $(CH_3)_3C$), 1.75 (4H, m, $OCH_2CH_2CH_3$), 3.15 (4H, m, $NHCH_2$), 3.27 (4H, d, ^2J = 13.2 Hz, $ArCH_2Ar$), 3.44 (4H, d, ^2J = 13.2 Hz, $ArCH_2Ar$), 3.98 (4H, t, ^3J = 7.8 Hz, $OCH_2CH_2CH_3$), 4.49 (2H, t, ^3J = 6.0 Hz, $NHCH_2$), 4.56 (4H, d, ^2J = 12.9 Hz, $ArCH_2Ar$), 4.58 (4H, d, ^2J = 13.2 Hz, $ArCH_2Ar$), 5.13 (4H, t, ^3J = 6.9 Hz, $ROCH_2CH_2OR'$), 5.29 (4H, t, ^3J = 7.5 Hz, $ROCH_2CH_2OR'$), 5.68 (2H, s, N*H*), 6.42 (4H, s, Ar*H*), 6.86 (4H, s, Ar*H*), 7.07 (4H, s, Ar*H*), 7.13 (4H, s, Ar*H*), 9.56 (2H, s, O*H*); MS (ES): *m*/*z* 1607 ($M + H^+$), 1629 ($M + Na^+$), 1645 ($M + K^+$).

Stability constant determinations

As cation complexation/decomplexation with **4** was slow on the NMR timescale, stability constants could be assessed by direct integration of the host and complex resonances. Spectra were recorded in the presence of various equivalents of each cation (in the range 0 to 5 equivalents). A *K* value was calculated for each spectrum recorded. The quoted stability constant for each ligand/cation system is the average of these *K* values. For all titration procedures, a solution of the receptor (600 µl) was prepared at a concentration of 0.001 mol dm^{-3} in the stated solvent system. Aliquots of cation or anion were added by gas-tight syringe from solutions made such that 1 mole equivalent was added in 20 µl.

Acknowledgements

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