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Calix[4]pyrroles bearing appended pyrenyl groups at the *meso*-positions on one side of the calix[4]pyrrole have been synthesised and characterised. These species act as hosts that exhibit a selective increase in their fluorescence intensity upon the addition of Pb^{2+} or Cu^{2+}. When excess chloride anion is added after subjecting the host to pre-complexation with Pb^{2+}, the cation-induced enhancement in fluorescence is sustained. On the contrary, no changes in fluorescence are observed when the calix[4]pyrrole host is first treated with chloride anion, followed by the addition of Pb^{2+}. These results are consistent with pre-complexation of Pb^{2+} not serving to inhibit the binding of chloride anion, while, by contrast, the initial interaction between a chloride anion and the calix[4]pyrrole cavity acts to inhibit the subsequent binding of Pb^{2+}, possibly due to anion-binding-based constraints on the conformational flexibility.

Keywords: calix[4]pyrrole; fluorophore appended; chemosensors; pyrene; CHEF

Introduction

Synthetic receptors that are capable of selective binding and recognition of anionic substrates are of great interest due to the importance of anions in the environment and biology (*1–6*). Nevertheless, the design and synthesis of anion receptors possessing high affinity and selectivity remain a challenging task due to the relatively complex nature of anionic species. Among the various neutral anion receptors reported in recent years, calix[4]pyrroles and their analogues have emerged as particularly attractive, in part because they are so readily accessible in terms of synthesis. Calix[4]pyrroles, for instance, may be obtained in one high-yielding step from commercially available starting materials and the octamethyl derivative is now commercially available. Not surprisingly, various modified calix[4]pyrroles have been prepared with the goal of generating derivatives with improved recognition properties (*7*). In this context, systems bearing diametrical strap on one side of the calix[4]pyrroles have attracted attention as being potentially superior systems for anion recognition. In contrast to most other calixpyrrole derivatives, these systems allow for a preorganisation of the anion-binding domain, a feature that has allowed for a fine-tuning of their selectivity and affinity (*8*). One key feature of the calix[4]pyrroles is that, unlike the calix[4]arenes, they are flexible and undergo a conversion from the normal 'resting' conformation, the so-called 1,3-alternate conformation, to a bowl-like cone conformation upon binding with anions. The spatial orientation of the *meso*-substituents undergoes a dramatic change as a consequence (Scheme 1).

If two or more fluorophores, such as pyrene, are introduced at the *meso*-positions of the calix[4]pyrrole (Scheme 1), this conformational motion could potentially be used to change the fluorescence properties of the molecule as a whole. This effect, which could be potentially exploited to produce so-called chemosensors ('sensors' for short), should be enhanced when auxiliary hydrogen bonding donor sites are introduced into the linker arm. Because the effects are largely conformation-based, the systems should give rise to greater substrate-induced changes in fluorescence than the more rigid pyrene-appended calix[4]arene systems that were reported early on (*9*). In fact, unlike these previous pyrene-functionalised systems, as well as the various other calix[4]pyrrole-based sensor systems reported to date, systems based on conformation-based changes in the orientation of chromophores are expected to combine directly an anion-binding event with a fluorescence change. In this paper, we report the synthesis and ion-binding properties of calix[4]pyrroles bearing pyrene moieties appended to one side of the calix[4]pyrrole. We also report the results of preliminary solution phase anion- and cation-binding studies and show that the systems in question can in fact act as viable sensors. As detailed below, in these systems ancillary functional groups have been incorporated into the linker

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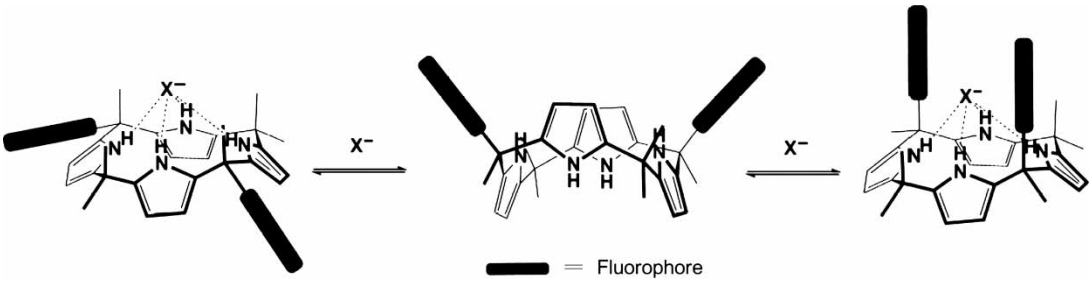


Scheme 1. Idealised conformational changes of pyrene-appended calix[4]pyrrole that are expected to occur upon anion binding.

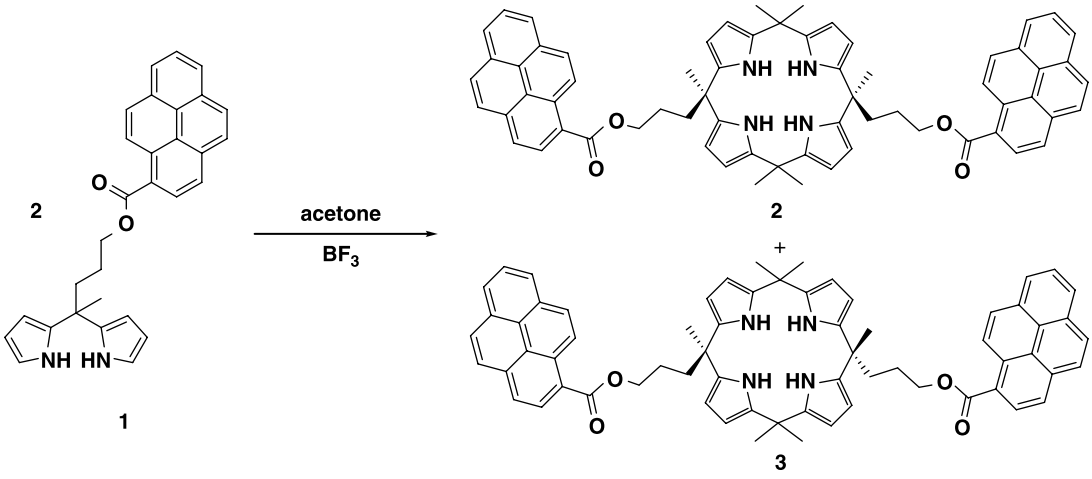
arm in order to gauge the effect, in any, that changes in the linker have on the system as a whole.

Results and discussion

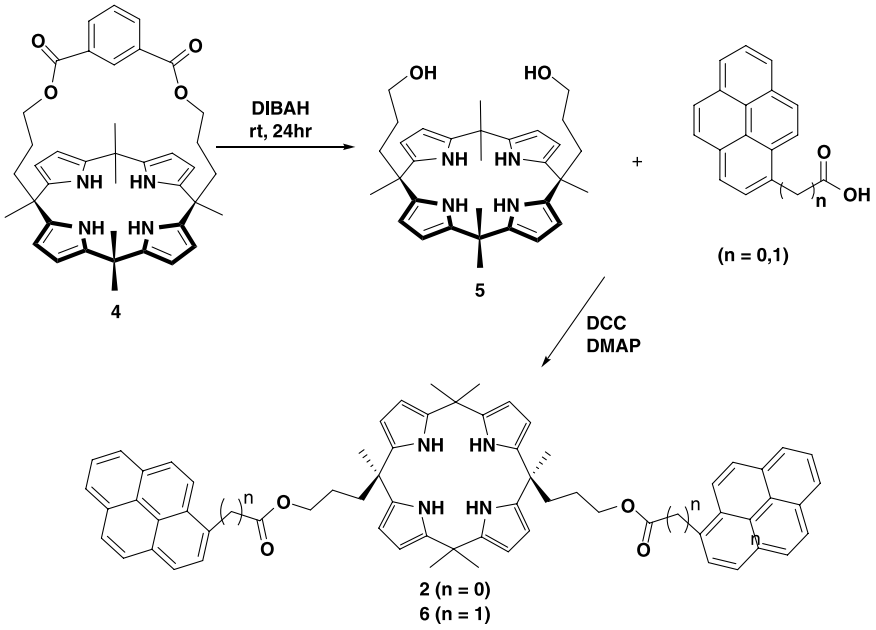
A key feature incorporated into the proposed receptors is the presence of flexible arms that strap the calix[4]pyrrole ring in a *cis*-fashion. Two different synthetic routes were attempted in an effort to access systems of this type. However, only one route gave rise to the desired product. The first route is shown in Scheme 2. Briefly, the pyrene-bearing dipyrromethane **1** was condensed with acetone to afford an isomeric mixture of compounds **2** and **3** which proved difficult to separate; indeed, all the attempted separations, including preparative TLC, failed. The alternative approach is shown in Scheme 3. In this case, a reductive cleavage of the diester functions of the strapped calix[4]pyrrole **4** was affected using DIBAH. This produced the bis-diol **5** in high yield, a species that was then condensed with pyrene carboxylic acid or α-pyrenyl acetic acid to afford receptors **2** or **6** in 22 and 15% yields, respectively. The identity of the compounds was confirmed by spectroscopic analysis including ^{1}H NMR spectroscopy and HR-MS.

Preliminary fluoride-anion-binding studies of systems **5** were carried out in DMSO-d_6 using proton NMR spectroscopy. This was done by titrating receptor **5** with fluoride anion studied in the form of its tetrabutylammonium salt. Here, a completely new set of signals were observed upon the addition of one equivalent of fluoride anion, a finding that is consistent with a 1:1 binding stoichiometry (cf. Figure 1). The results are clearly consistent with slow complexation/decomplexation kinetics.

Typical changes in the signals seen during the titration include the following: (*1*) the pyrrole N—H proton signals appearing originally at 9.23 in the absence of fluoride anion were shifted to 12.75 ppm in the presence of fluoride anion. On the other hand, the β-pyrrolic proton signals appearing originally at 5.68 ppm were found to be shifted to 5.40 ppm. Likewise, the —OH protons at 4.37 ppm were shifted to 4.31 ppm as would be expected given the lack of interaction with the bound anion. It is worth reiterating that, unlike *meso*-octamethyl calix[4]pyrrole, system **5** displays slow binding equilibrium when titrated with fluoride anion. On the basis of this and the other observations noted above, it is concluded that the anion must bind within the pocket generated by the calix[4]pyrrole and the two hydroxyl groups that are hydrogen bonded each other. Thus, the participation of the hydroxyl groups in the binding process is excluded.



Scheme 2.



Scheme 3.

Titration of receptor **5** with acetate anion studied in the form of its tetrabutylammonium salt gave similar results as those observed with fluoride anion. For example, the pyrrole N—H protons were shifted to 11.11 ppm in the presence of acetate anion. Interestingly, the –OH proton signal was shifted downfield from 4.37 ppm to 4.44 ppm. This observation indicates that the hydroxyl groups participate in the anion-binding process of the acetate anion.

Additional quantitative studies of the anion-binding properties of **5** were made using isothermal titration calorimetry (ITC). An advantage of this method is that it allows for the study of recognition events at concentrations that are lower than those required for NMR spectroscopic analyses. ITC also permits the accurate determination of much higher binding affinities than do NMR-based methods. Unfortunately, we have been unable to obtain reliable binding constant data for fluoride anion binding. However, we were able to determine binding constants (K_a) for chloride, acetate, phosphate and sulphate anions (Table 1).

The association constant obtained from ITC measurement in CH_3CN/DMSO (3%) for the formation of [**3**·Cl^-] was $1.72 \times 10^5\,M^{-1}$, while that for [**3**·AcO^-] was $2.36 \times 10^6\,M^{-1}$. On the other hand, the association constant for the complex formation of [**7**·Cl^-] was $2.13 \times 10^6\,M^{-1}$, while that of [**7**·AcO^-] was $4.39 \times 10^5\,M^{-1}$. It is clear that the ester-strapped calix[4]pyrrole bearing well-preorganised binding domain exhibits a higher affinity for spherical-shaped anion. On the other hand, the non-spherical multi-oxo anions showed a higher affinity for the rather flexible receptor **5**.

The anion-binding properties of systems **2** and **6** were studied using fluorescence methods. Since the pyrene-appended calix[4]pyrroles are conformationally more flexible than the congeneric calix[4]arene systems, these fluorophore-functionalised systems were expected to exhibit a rather dynamic fluorescence response upon guest binding.

Preliminary fluoride-anion-binding studies of compound **2** carried out in CD_2Cl_2 using proton NMR spectroscopy were consistent with fast complexation/decomplexation kinetics as shown in Figure 2. Specifically, the pyrrole N—H signal shown at 7.09 ppm disappeared upon the addition of one equivalent of fluoride anion.

Since compounds **2** and **6** possess ester functions within the linker, it was considered likely that metal ions could interact with these linkers, as seen in the case of calix[4]arenes bearing ester functionality (*10*). In order to obtain insight into the interaction between the putative metal–ion guests and compound **2**, the fluorescence changes seen upon the addition of various metal ions were examined. When excited at 343 nm, compound **2** displays emission features at 391 and 410 nm that are typical of the monomeric emission of pyrene. On the other hand, addition of Cu^{2+} and Pb^{2+} in particular gave rise to a large fluorescence enhancement as shown in Figure 3. This enhancement could be explained by a chelation enhanced fluorescence (CHEF) effect caused by metal–ion

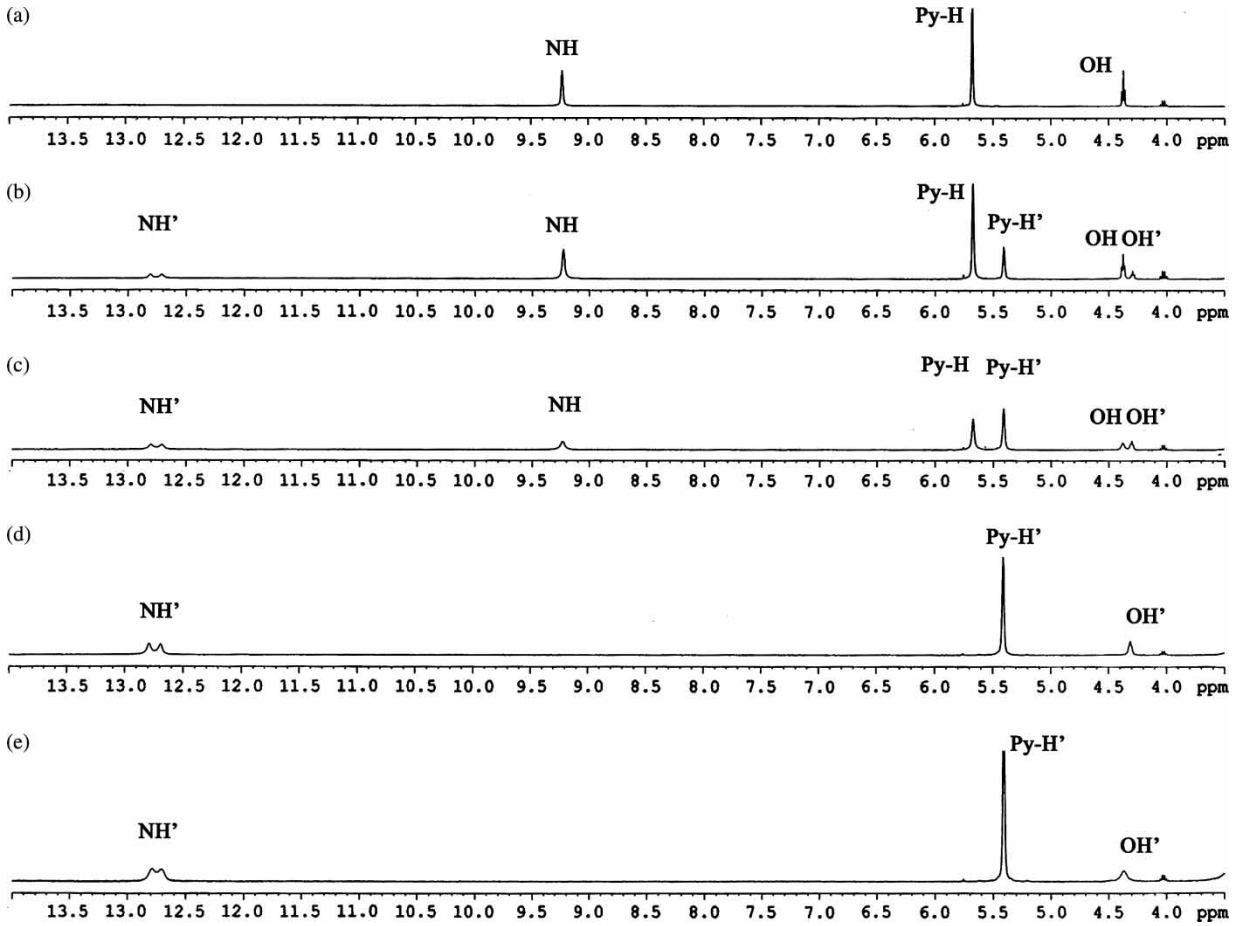


Figure 1. Titration of receptor **5** with fluoride anion (as its tetrabutylammonium salt) in DMSO-d_6. ([**5**] = 4.26 mM). (a) Free, (b) 0.25 equiv., (c) 0.64 equiv., (d) 1.04 equiv. and (e) 2.0 equiv., respectively.

chelation to the carbonyl oxygen atoms of **2** (*11*). This observation indicates that the fluorescence of free host **2** must be significantly quenched by PET process from calix[4]pyrrole to pyrene (*12*). Upon metal–ion complexation, however, the lone-pairs on the carbonyl oxygen are no longer available, causing the observed CHEF effect.

The calculated overall affinity constant for Pb^{2+} is 5.90×10^5 and $6.6 \times 10^5\,M^{-1}$ for Cu^{2+}. The comparably large CHEF effect is observed only for Pb^{2+} and Cu^{2+}. Other smaller metal ions including Li^+, Na^+, K^+, Mg^{2+}, Sr^{2+} and Ca^{2+} do not show a significant CHEF effect upon binding.

A Job plot shown in Figure 3 corresponds to the binding stoichiometry 1/2 (host/guest) binding mode (*13*), which can be explained by assuming that each carbonyl group holds a metal ion separately while the host adopt stable 1,3-alternate conformation. Although the two carbonyl groups bind to single metal ion simultaneously, the molecular rigidity will increase and subsequently contribute to the fluorescence enhancement. However, current results clearly indicate the former is operating.

When excess Cl^- (20 equiv. as its tetrabutylammonium salt) was pretreated with **2** before adding excess Pb^{2+}, no CHEF effect is observed (Figure 4); probably, this is due to a salting out of $PbCl_2$ from the solution. On the other hand, when a Pb^{2+}-saturated solution of **2** was treated with excess TBACl, the enhanced fluorescence was sustained. These results confirm that the Pb^{2+} as well as Cu^{2+} are coordinated to the two carbonyl oxygen, permitting the CHEF effect to be observed.

Since, compound **2** does not exhibit excimer formation upon treatment with either metal ion or anion, we prepared compound **6** that has an additional methylene unit in the linker; it too was studied for its metal–ion-binding properties. Unlike what proved true for compound **2**, excitation of free host **6** at 343 nm gives rise to both monomer emission at 397 nm and excimer emission at 472 nm, suggesting that the two forms are in dynamic equilibrium as shown in Figure 5. Titration with Pb^{2+} ion

Table 1. Association constants, K, and thermodynamic parameters for the binding of chloride, acetate, phosphate and sulphate anions by hosts **5**, the ester-strapped calix[4]pyrrole **4**, and *meso*-octamethyl calix[4]pyrrole as measured by ITC at 25°C using the corresponding tetrabutylammonium salts in CH_3CN/DMSO (3%).

	5				**4**				*meso*-octamethyl calix[4]pyrrole			
Anions	ΔG (kcal)	ΔH (kcal)	$T\Delta S$ (cal)	K (M^{-1})	ΔG (kcal)	ΔH (Kcal)	$T\Delta S$ (cal)	K (M^{-1})	ΔG (kcal)	ΔH (kcal)	$T\Delta S$ (cal)	K (M^{-1})
Cl^-	−7.02	−8.53	−5.14	1.72×10^5	−8.45	−7.47	3.49	2.13×10^6	−6.72	−6.59	0.427	1.02×10^5
AcO^-	−8.55	−9.40	−2.92	2.36×10^6	−7.57	−9.43	−6.36	4.39×10^5	−7.16	−9.23	−7.06	2.17×10^5
$PO_4H_2^-$	−7.09	−7.42	−1.1	1.94×10^5	−5.66	−1.60	−35.3	1.7×10^4				
SO_4H^-	−3.91	−7.13	−11.0	8.04×10^2	−3.25	−8.32	−17.3	1.2×10^2				

gives rise to a gradual shift in the equilibrium from excimer to monomeric species. Figure 6 shows the intensity ratio (I_{mono}/I_{ex}) with varying concentration of **6** and provides support for the proposed intermolecular nature of the interaction.

These results indicate that metal–ion complexations shifts the equilibrium towards a monomeric complex possibly as the result of simultaneous complexation of Pb^{2+} with two carbonyl oxygens (Scheme 5).

In summary, we have demonstrated that the pyrene-armed calix[4]pyrroles could be good fluorescence receptor models for cations and anions. The property of the connecting arms between pyrenyl group and *meso*-carbon directs the nature of the interaction of the two appended pyrene units. These systems are thus expected to be potentially useful in the selective fluorometric detection of Cu^{2+} or Pb^{2+} ions and molecular logic devices that may be controlled by variations in cation and anion concentrations. Accordingly, a new series of compounds bearing rigid connecting arms are under preparation and they and their binding properties will be reported in due course.

Experimental

Proton NMR spectra (400 MHz, Bruker DPX-400) were recorded using TMS as the internal standard. High- and low-resolution FAB mass spectra were obtained on an AUTO SPEC M-363 high-resolution mass spectrometer. Column chromatography was performed over silica gel (Merck, Whitehouse Station, NJ, USA, 230–400 mesh). Pyrrole was distilled at atmospheric pressure from CaH_2. All other reagents were obtained from Aldrich and used as received unless noted otherwise. Strapped calix[4]pyrrole **4** was synthesised according to the literature procedure (*8a*). ITC measurements were performed as follows: solutions of the chosen receptor in rigorously dry acetonitrile were made up so as to provide a receptor concentration range of ~1.0 mM. These solutions were then individually titrated with the appropriate alkylammonium salts at 30 ± 0.01°C. The original heat pulses were normalised using reference titrations carried out using the same salt solution but pure solvent, as opposed to a solution containing the receptor.

cis-*5,10-Bis-(3-hydroxypropyl) calix[4]pyrrole (5)*

Compound **4** (0.1 g, 0.15 mmol) was dissolved in THF (50 ml) and the temperature was cooled to 0°C. Then, DIBAH (1.50 ml, 1.5 mmol, 1.0 M solution in hexanes) was added portionwide and the mixture was stirred for 6 h at room temperature. The mixture was combined with water (50 ml) and extracted with ethyl acetate. The organic layer was then washed with water and

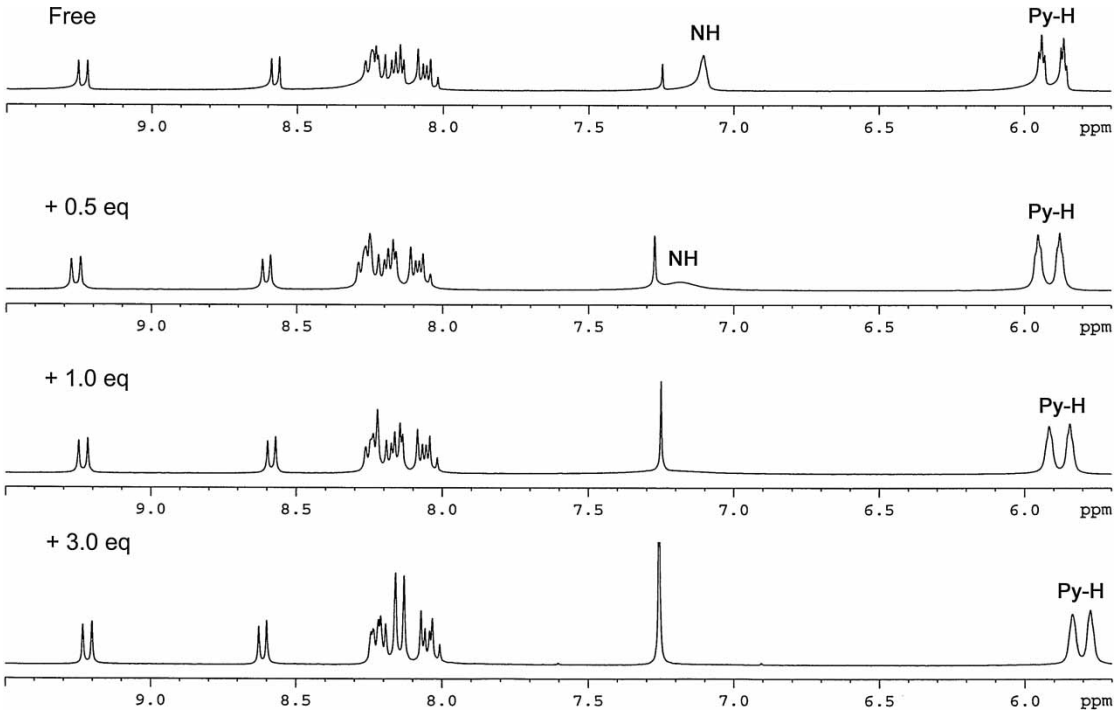


Figure 2. ^{1}H NMR titration of **2** with fluoride anion (as its tetrabutylammonium salt) in $CDCl_3$. [**2**] = 1.65×10^{-3} M.

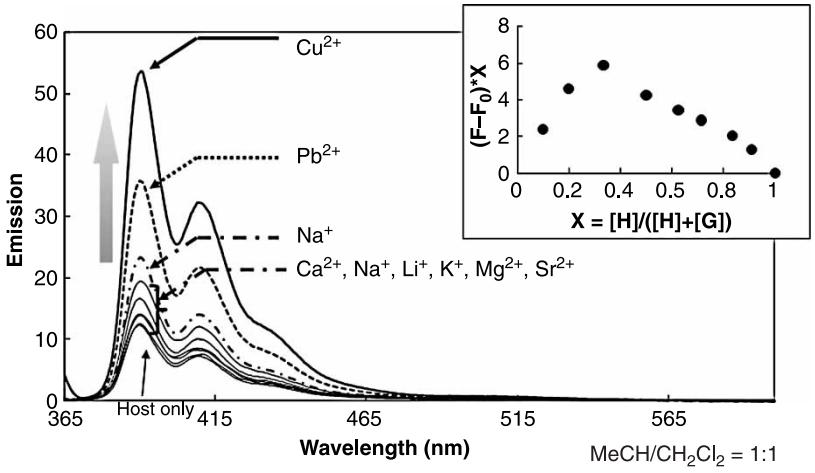


Figure 3. Changes in fluorescence emission spectra observed upon the addition of various metal cations as their perchlorate salts. [**2**] = 6.67×10^{-7} M in CH_3CN; a 1000-fold excess of the metal ion was added in each experiment. The inset graph is the Job plot for the Pb(II) binding.

dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and resulting solid was washed with THF and recrystallised in methanol. Yield 90% (67 mg); ^{1}H NMR (DMSO-d_6) δ 9.23 (br s, 4H, NH), 5.68 (d, 8H, $J = 1.88$ Hz, pyrrolic-H), 4.37 (t, 2H, $J_{b-c} = 5.14$ Hz, OH), 3.31 (q, 4H, $J_{b-d} = 16.8$ Hz, CH_2), 1.87–1.83 (m, 4H, CH_2), 1.52 (s, 6H, CH_3), 1.48 (s, 6H, CH_3), 1.46 (s, 6H, CH_3), 1.28–1.21 (m, 4H, CH_2); ^{13}C NMR (DMSO-d_6) δ 25.22, 28.36, 28.47, 30.37, 34.89, 37.82, 38.23, 102.07, 102.91, 137.90, 138.90; MALDI-TOF MS calcd for $C_{32}H_{44}N_4O_2$ *m/z* 516.35, found 517.50 ($M + H^+$), 539.49 ($M + Na^+$), 555.46 ($M + K^+$).

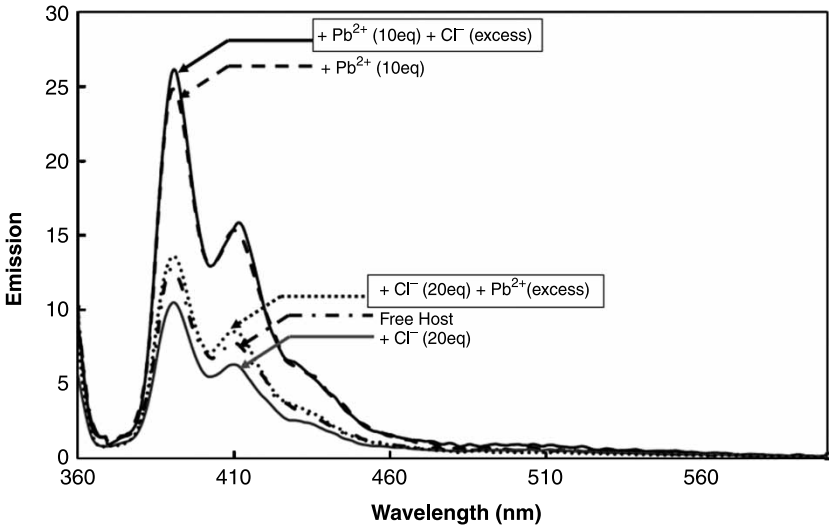
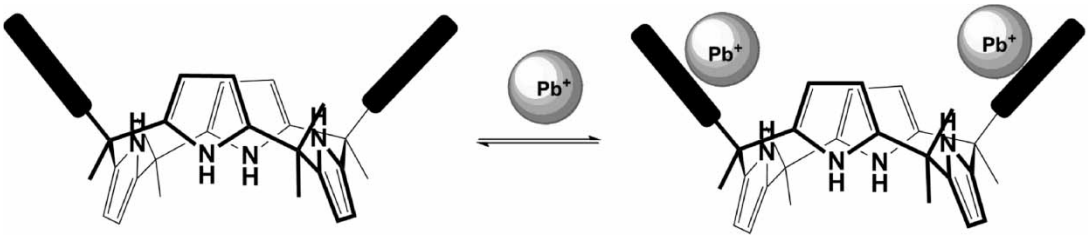


Figure 4. Change in the fluorescence emission spectra of host **2** observed upon the addition of Pb^{2+} and chloride anion (TBACl) as the result of two separate sequences of addition [**2**] = 6.67 × 10^{-7} M (in CH_3CN/CH_2Cl_2 = 1/1).



Scheme 4.

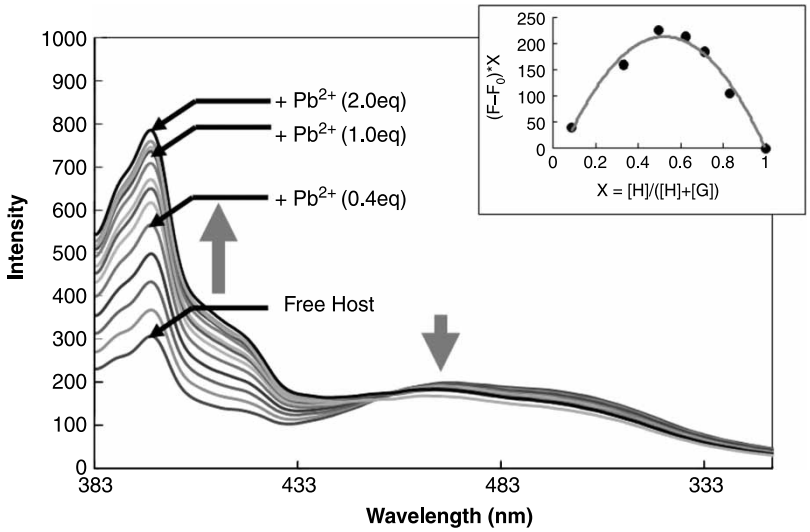


Figure 5. Changes in the fluorescence emission spectra seen upon the addition of Pb^{2+} (as its perchlorate salt) to receptor **6**. [**6**] = 5.08 × 10^{-7} M in CH_3CN/CH_2Cl_2 (1/1). λ_{ex} = 343 nm. The inset graph is the Job plot for the Pb(II) binding.

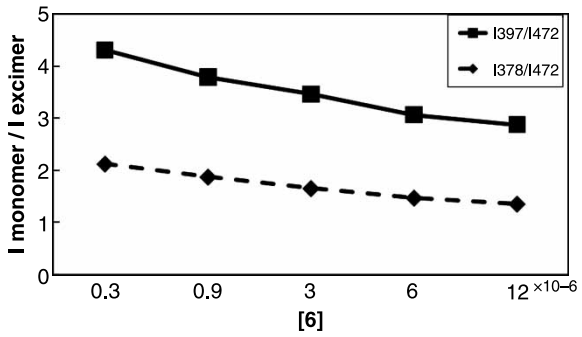
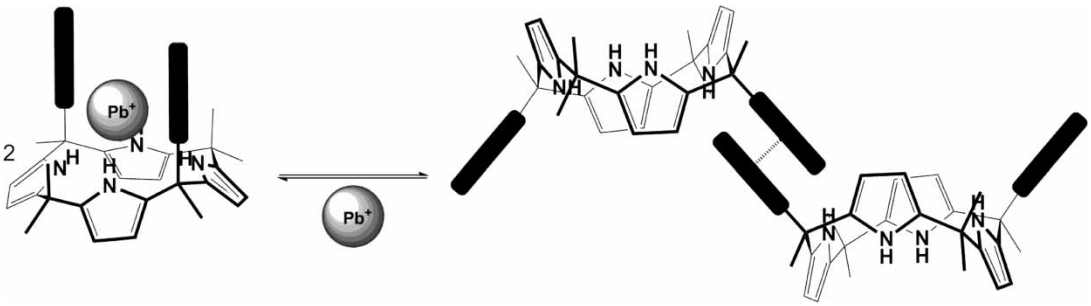


Figure 6. Change in the intensity ratio ($I_{monomer}/I_{excimer}$) for **6** as a function of varying the concentration. [**6**] = 1.2×10^{-5}–3.0×10^{-7} M in CH_3CN/CH_2Cl_2 (1/1).



Scheme 5.

Benzopyrene-appended calix[4]pyrrole (2)

Compound **5** (0.1 g, 0.19 mmol), 1-pyrenylcarboxlic acid (0.25 g, 0.12 mmol), DCC (0.25 g, 0.13 mmol) and DMAP (0.14 g, 0.12 mmol) was dissolved in THF (100 ml). The whole mixture was then stirred for 12 h at room temperature. Then, the solution was passed through short silica column with several washing with methylene chloride. The solvent was removed and the resulting solid was purified by prep. TLC (CH_2Cl_2). Yield 27% (50 mg); ^{1}H NMR ($CDCl_3$) δ 9.24 (d, 2H, J = 9.45 Hz, pyrene-H), 8.58 (d, 2H, J = 8.13 Hz, pyrene-H), 8.27–8.21 (m, 6H, pyrene-H), 8.18–8.15 (m, 4H, pyrene-H), 8.09–8.03 (m, 4H, pyrene-H), 7.08 (br s, 4H, NH), 5.90 (t d, 8H, J = 11.35 Hz, pyrrolic-H), 4.39 (t, 4H, J = 6.34 Hz, CH_2), 2.12–2.08 (m, 4H, CH_2), 1.75–1.72 (m, 4H, CH_2), 1.52 (s, 6H, CH_3), 1.49 (s, 6H, CH_3), 1.43 (s, 6H, CH_3); ^{13}C NMR($CDCl_3$) δ 24.10, 26.25, 28.99, 29.41, 35.23, 37.19, 38.59, 65.43, 102.96, 103.95, 123.73, 124.11, 124.21, 126.16, 126.28, 126.31, 127.17, 128.27, 129.42, 129.61, 130.38, 131.01, 131.10, 134.27, 136.95, 138.65; MALDI-TOF MS calcd for $C_{66}H_{60}N_4O_4$ *m/z* 972.46, found 973.55(M + H^+).

Benzopyrene-incorporated calix[4]pyrrole (6)

Compound **5** (0.1 g, 0.19 mmol), 1-pyrenylacetic acid (0.3 g, 0.12 mmol), DCC (0.25 g, 0.13 mmol) and DMAP (0.14 g, 1.16 mmol) were treated identically as for the synthesis of **2**. Yield 18% (35 mg); ^{1}H NMR($CDCl_3$) δ 8.25 (d, 2H, J = 9.26 Hz, pyrene-H), 8.17–7.90 (m, 16H, pyrene-H), 6.85 (br s, 4H, NH), 5.62 (d, 8H, J = 13.2 Hz, pyrrolic-H), 4.33 (s, 4H, CH_2), 3.97 (t, 4H, J = 6.25 Hz, CH_2), 1.67–1.64 (m, 4H, CH_2), 1.49 (m, 4H, CH_2), 1.42 (s, 6H, CH_3), 1.36 (s, 6H, CH_3), 1.28 (s, 6H, CH_3). ^{13}C NMR ($CDCl_3$) δ 23.77, 25.97, 26.31, 28.80, 29.46, 30.31, 30.97, 35.08, 36.85, 38.27, 39.69, 65.26, 102.83, 103.73, 123.22, 124.76, 124.87, 125.04, 125.12, 125.25, 125.94, 127.26, 127.39, 128.00, 128.16, 128.34, 129.40, 130.78, 130.82, 131.32; MALDI-TOF calcd for $C_{68}H_{64}N_4O_4$ (*m/z*) 1000.49, found 1001.49 ($M^+ + H^+$).

Acknowledgements

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