Chromogenic Ligands for Lithium Based on Calix[4]arene† Tetraesters Bearing Nitrophenol Residues

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Three novel chromogenic calix[4]arene tetraesters bearing nitrophenol residues which dramatically change their UV–VIS absorbance spectra upon complexation with metal ions have been investigated. Upon addition of metal perchlorates such as lithium or sodium to a solution of the calixarene in tetrahydrofuran, in the presence of a base, a colour change from near colourless to yellow occurs. The colour density is dependent on metal perchlorate concentration and can be monitored by UV–VIS spectroscopy. All three compounds were found to be lithium selective with a 10–40 fold selectivity for lithium against sodium. No colour change was noted in the absence of a base. From two-phase studies, it has been demonstrated that all three ligands have the ability to extract metal ions from an aqueous phase into an immiscible organic phase (butan-1-ol) which had been made basic by the addition of the lipophilic base triodecylamine, with a colour change from near colourless to yellow occurring in the organic phase. The deprotonated calixarene metal ion complex was found to diffuse into the aqueous phase with time, with the rate of diffusion being strongly dependent on the lipophilic nature of the calixarene backbone.

Calixarenes have evoked much interest in recent years due to their ion binding properties and relative ease of synthesis.[1,2] Ionophoric properties can be imparted to these molecules by the addition of ligating side chains at one of the many sites available for structural modification. Several successful potentiometric sensors have been reported which employ a calixarene as the ion-sensing agent in the selective membrane. However, over recent years increasing interest has been shown in the development of chemical sensors which employ optical transduction.[3,4]

In particular, the detection of clinically important species such as lithium, sodium and potassium by optical methods has commanded much recent attention. Initial success in this area was reported with chromogenic crown ethers and spherands,[5–7] and more recently with modified calixarenes.[8–13] The attachment of ionisable chromogenic groups adjacent to the polar cavity of these molecules produced materials which upon complexation with a metal cation caused a deprotonation of the chromogenic group which in turn resulted in a dramatic change in the absorbance spectrum.

Similar attempts to design materials for the analysis of lithium and sodium employing fluorescent optical transduction have been reported for cyclic and non-cyclic polyethers,[14,15] and calix[4]arenes,[16,17] with possible improvements in limits of detection over potentiometric and absorbance measurements.

Calix[*n*]arene (*n* = 4, 5, 6) derivatives (*e.g.* esters, ketones) and oxocalixarenes have been investigated as ionophores through their incorporation into poly(vinyl chloride) (PVC) membranes and have produced ion-selective electrodes for sodium, caesium, and potassium, with the sodium selective electrodes having particularly good characteristics.[18–23] It was anticipated that by incorporation of an ionisable chromophoric group in the vicinity of the ester podands of a calix[4]arene tetraacetate, a compound which would have the inherent metal binding capacity of the parent calixarene, and which would show a dramatic change in absorbance spectrum on complexation, could be produced. Three such compounds (**1**–**3**) have now been synthesised, the ionisable chromophore in each case being provided by a 3-hydroxy-4-nitrobenzyl moiety. Compound **2**, with the C_{18} alkyl chain on the *para*-position, was used to exploit lipophilicity differences. All three compounds were synthesised by reaction of the appropriate acid chloride with 3-hydroxy-4-nitrobenzyl alcohol.

Experimental

Materials.—Tetrahydrofuran (THF) was obtained from Fluka Chemika. Butan-1-ol was purchased from Riedel De Haen. Deuteriated chloroform, sodium thiocyanate, the bases morpholine and tridodecylamine (TDDA), and the perchlorates of lithium, sodium and potassium were obtained from the Aldrich Chemical Company. The perchlorate solutions were made up in Milli-Q water. NMR (*J*-values in Hz), IR and UV–VIS spectra were obtained with a Bruker AC-400 spectrometer, a Perkin-Elmer 983G spectrophotometer, and a Hewlett-Packard 8452A Diode Array Spectrophotometer, respectively.

Synthetic Details.—$1^5,3^5,5^5,7^5$-*Tetra*-tert-*butyl*-$1^2,3^2,5^2,7^2$-*tetra*(3-*hydroxy*-4-*nitrobenzyloxycarbonylmethoxy*)-1,3,5,7-*tetra*[1,3]*benzenacyclooctaphane* (*ligand* **1**). The tetraacid chloride (**4**) (1.0 g, 1.01 mmol) was dissolved in dry THF (10 cm^3) and added dropwise, under nitrogen, to a stirred solution of 3-hydroxy-4-nitrobenzyl alcohol (0.77 g, 4.55 mmol) and triethylamine (0.63 cm^3, 4.55 mmol). The mixture was stirred at room temp. for 24 h, at which stage all volatiles were removed. The resulting residue was dissolved in methylene chloride (50 cm^3) and washed with several portions of distilled water. The organic layer was separated, dried and volatiles removed to give 1.2 g of the tetra(3-hydroxy-4-nitro)benzyl ester (ligand **1**). Coloured impurities were removed by charcoal treatment in hot chloroform. Pure product was obtained as a pale yellow solid (0.63 g, 76% yield) by column chromotography on silica gel, using methylene chloride as eluent (R_f 0.60); m.p. 73–76 °C (Found: C, 64.0; H, 5.75; N, 3.4. $C_{80}H_{84}N_4O_{24}$ requires: C, 63.84; H, 5.70; N, 3.79%); ν_{max}(KBr)/cm^{-1} 3593 (OH), 1756 (CO) and 1477 (NO_2); δ_H($CDCl_3$) 0.84 (18 H, s, Bu^t), 1.34 (18 H, s, Bu^t), 3.30 (4 H, 2 overlapping d, H_B, $ArCH_2Ar$), 4.59 (4 H, br s,

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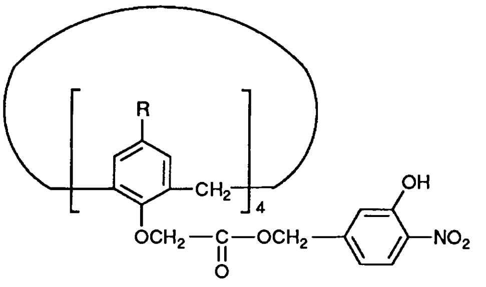
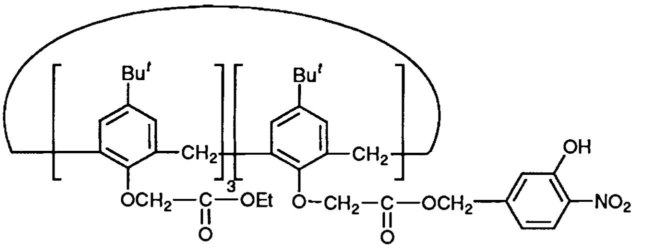
† 1,3,5,7-Tetra[1,3]benzenacyclooctaphane.



1 (ligand 1) R = Bu^t
2 (ligand 2) R = $[CH_2]_{17}CH_3$



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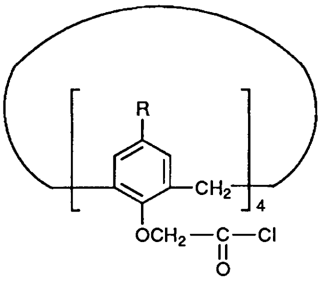

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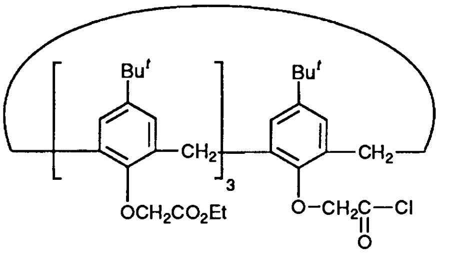

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ArOH), 4.76 (8 H, s, OCH$_2$), 4.98, 5.13 (2 H, d, J_{AB} 13.0, H$_A$ ArCH$_2$Ar), 5.23 (8 H, s, OCH$_2$Ar), 6.85 (4 H, d, ArH), 7.01–7.18 (12 H, m, ArH) and 8.06 (4 H, d, ArH); δ_C(CDCl$_3$) 30.94, 31.29 [C(CH$_3$)$_3$], 31.59 (ArCH$_2$Ar), 33.75, 34.25, [C(CH$_3$)$_3$], 63.72 (OCH$_2$CO), 68.16 (OCH$_2$Ar), 116.82, 117.91, 119.912 (Ar of Bz), 125.26, 125.58, 125.71, 126.08 (Ar), 128.98, 130.88 (Ar of Bz), 133.32, 133.19, 134.63, 135.20, 146.32, 154.91, 155.21 (Ar) and 169.78 (CO).

1^5,3^5,5^5,7^5-*Tetraoctadecyl*-1^2,3^2,5^2,7^2-*tetra*(3-*hydroxy*-4-*nitrobenzyloxycarbonylmethoxy*)-1,3,5,7-*tetra*[1,3]-*benzenacyclooctaphane* (*ligand* **2**). The reaction mixture consisted of *p*-octadecylcalix[4]arene (0.50 g, 0.35 mmol), prepared following the method described by Böhmer:[24] anhyd. potassium carbonate (0.29 g, 2.1 mmol), ethyl bromoacetate (0.47 g, 2.8 mmol) and anhyd. acetone (15 cm^3). This was refluxed under nitrogen for 96 h, after which all volatiles were removed at room temp. The resulting residue was taken up in dichloromethane (25 cm^3) and HCl (25 cm^3; 1 mol dm^{-3}). The organic layer was separated, dried and volatiles removed to give pale brown solid tetraethylester calix[4]arene (0.65 g), which was chromatographed on neutral alumina using 50% light petroleum–methylene chloride as eluent to give tetraethylester calix[4]arene (0.37 g, 60%) as a very pale brown solid, m.p. 49–51 °C (Found: C, 74.7; H, 10.0. $C_{116}H_{192}O_{12}\cdot CH_2Cl_2$ requires C, 75.40; H, 10.41%); ν_{max}(KBr)/cm^{-1} 1757br (CO).

All (0.37 g) of this compound was then refluxed for 2 h with potassium hydroxide (0.40 g, 7.1 mmol) in ethanol (5 cm^3), after which all volatiles were removed. To the residue was then added aq. HCl (5 cm^3; 10 mol dm^{-3}) to give a colourless solid which was then washed well with distilled water and left to dry at room temp. for 72 h to give colourless carboxylic acid (0.35 g) (m.p. 68–71 °C); ν_{max}(KBr)/cm^{-1} 1737. This compound was refluxed under nitrogen with thionyl chloride (5 cm^3) for 2 h, after which all volatiles were removed to give grey solid acid chloride (0.36 g). This amount of tetraacid chloride (0.2 mmol) was dissolved in dry THF (5 cm^3) and added dropwise under nitrogen with stirring to 3-hydroxy-4-nitrobenzyl alcohol (0.15 g, 0.9 mmol) and triethylamine (0.12 cm^3, 0.9 mmol) in THF (5 cm^3). The mixture was stirred at room temp. for 24 h at which stage all volatiles were removed. The resulting residue was dissolved in methylene chloride (10 cm^3) and HCl (5 cm^3; 1 mol dm^{-3}). After washing twice with distilled water, the organic layer was separated, dried and volatiles removed to give tetra(3-hydroxy-4-nitro)benzyl ester (0.46 g) (ligand **2**). Pure product ligand **2** was obtained as a yellow solid (m.p. 64–65 °C) by chromatography on neutral alumina using 15% light petroleum–methylene chloride as eluent (0.40 g, 87%) (Found: C, 70.9; H, 8.5; N, 2.1. $C_{136}H_{196}N_4O_{24}\cdot\frac{1}{2}CH_2Cl_2$ requires C, 70.86; H, 8.58; N, 2.42%); ν_{max}(KBr)/cm^{-1} 3500 (OH), 1753 (CO) and 1465 (NO$_2$).

1^5,3^5,5^5,7^5-*Tetra*-tert-*butyl*-1^2-(3-*hydroxy*-4-*nitrobenzyloxycarbonylmethoxy*-3^2,5^2,7^2-*tri*(*ethoxycarbonylmethoxy*) 1,3,5,7-*tetra*[1,3]*benzenacyclooctaphane* (*ligand* **3**). To a stirred solution of 3-hydroxy-4-nitrobenzyl alcohol (0.76 g, 4.49 mmol) and triethylamine (0.62 cm^3, 4.49 mmol) in dry THF, a solution of monoacid chloride triethylester (**5**) (3.0 g, 3.04 mmol) in THF (10 cm^3) was added dropwise. The mixture was stirred at room temp. under a nitrogen atmosphere for 24 h. After this time volatiles were removed to give a dark yellow residue. This solid was dissolved in methylene chloride and washed with distilled water, brine and 5% sulfuric acid. The organic layer was separated, dried and volatiles removed under reduced pressure to afford 2.29 g (75%) of mono(3-hydroxy-4-nitro)benzylester-calix[4]arene. This product was purified by column chromatography on silica gel using 25% light petroleum methylene chloride as eluent to afford 1.42 g (62%) of ligand **3** as a pale yellow solid (R_f 0.62); m.p. 117–119 °C (Found: C, 69.5; H, 7.25; N, 1.2. $C_{65}H_{81}NO_{15}$ requires C, 69.93; H, 7.31; N, 1.26%); ν_{max}(KBr)/cm^{-1} 1752br (CO); δ_H(CDCl$_3$) 1.00 (9 H, s, Bu^t), 1.17 (27 H, s, Bu^t), 1.31 (9 H, t, J 5.0, CH$_2$CH_3), 3.24 (4 H, 2 overlapping d, H$_B$, ArCH$_2$Ar), 4.21 (6 H, m, CH_2CH$_3$), 4.71–4.84 (4 H, m, OCH$_2$), 4.86 (4 H, 2 d, H$_A$, ArCH$_2$Ar), 4.98 (2 H, s, OCH$_2$), 5.33 (2 H, s, OCH$_2$), 6.90 (4 H, s, ArH), 6.89 (4 H, d, J 1.5, ArH), 7.42 (1 H, d, ArH), 7.45 (1 H, s, ArH) and 8.06 (1 H, d, ArH).

Effect of Complexation on UV–VIS Absorbance.—Solutions of the ligands were made up in THF (ligands **1** and **2** at 5 × 10^{-5} mol dm^{-3}, and ligand **3** at 10^{-4} mol dm^{-3}). Aliquots (2.5 cm^3) of these solutions were taken and morpholine was added in the following amounts: 20 mm^3 for ligands **1** and **2**; 45 mm^3 for ligand **3**. Incremental concentrations of the aqueous metal perchlorates were added to give final concentrations in the range 10^{-1}–10^{-6} mol dm^{-3}. The UV–VIS spectra of the solutions were obtained between 800 and 300 nm. In order to determine selectivity coefficients in this one-phase system, a series of

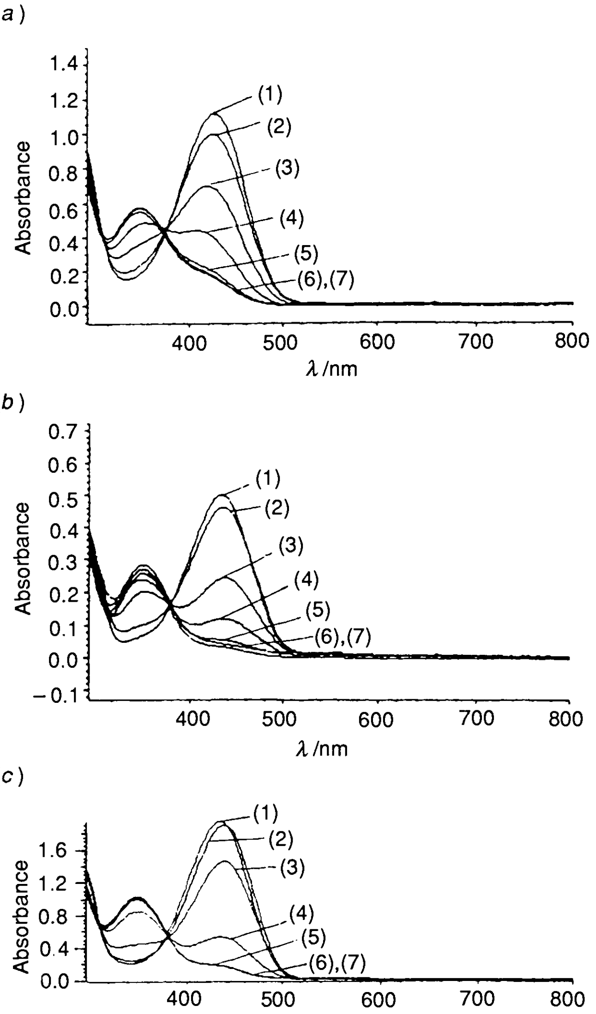

Fig. 1 One-phase investigation of changes in the absorbance spectrum of 2.5 cm^3 of a 5 × 10^{-5} mol dm^{-3} solution of: (*a*) ligand **1**, and (*c*) ligand **2** in THF, with 20 mm^3 morpholine; and (*b*) 10^{-4} mol dm^{-3} ligand **3** in THF, with 45 mm^3 morpholine, upon addition of aq. $LiClO_4$—with final concentrations of 0.1 (1), 10^{-2} (2), 10^{-3} (3), 10^{-4} (4), 10^{-5} (5), 10^{-6} (6) and 0 mol dm^{-3} (7)

experiments was set up as above, with the final lithium perchlorate concentration being varied in the range 10^{-1}–10^{-6} mol dm^{-3}, in a fixed background concentration *i.e.* 10^{-2} or 10^{-3} mol dm^{-3}, of interfering ion in the form of sodium perchlorate. Spectra were obtained from 800 to 300 nm.

For two-phase experiments, TDDA (20 mm^3) was added to aliquots (2.5 cm^3) of 5 × 10^{-5} mol dm^{-3} solutions of each of the ligands made up in butan-1-ol. To these, 2.5 cm^3 of water was added. Incremental concentrations of metal perchlorates were then added to the lower, aqueous phase to give final aqueous phase concentrations in the range 10^{-1}–10^{-6} mol dm^{-3}. Spectra were taken of both phases.

Results and Discussion

A number of parameters should be considered when setting up experiments involving these types of chromogenic calixarenes. The base must not be too strong, or deprotonation of the chromogenic group attached to the calixarene will occur in the absence of the metal ions. With the bases morpholine and TDDA, a slight colour change in tetrahydrofuran was noticed after the addition of base, indicating that the bulk of the ligand remained in the protonated form in both cases. The UV–VIS spectrum of the ligand in THF with morpholine before the addition of $LiClO_4$, is shown as the lowest trace in Fig. 1(*a*) and (*b*) confirming that very little deprotonation has occurred.

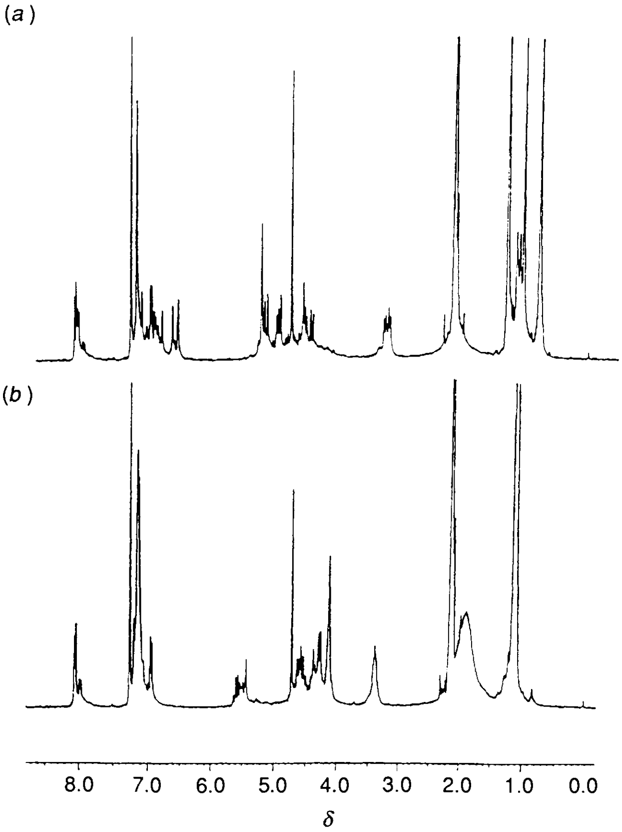

Fig. 2 ^{1}H NMR spectra of the free and complexed form of ligand **1** in $CDCl_3$ at room temp.: (*a*) R = [NaSCN]/[**1**] = 0; (*b*) R = 1; where [**1**] = 5.0 × 10^{-3} mol dm^{-3} in $CDCl_3$. An aliquot from a 1.0 mol dm^{-3} solution of NaSCN in CD_3OD was added directly to a $CDCl_3$ solution of **1** in an NMR tube (see text for interpretation).

Upon addition of lithium perchlorate in the presence of morpholine to the colourless solutions of ligands **1** and **3** in THF, a clear yellow colour was immediately observed, with the density of the colour being dependent on the concentration of the metal perchlorate added. From the UV–VIS spectra [Fig. 1(*a*) and (*b*)], an absorbance maximum for the coloured complex at 425 nm and an isobestic point at 375 nm can be clearly identified. The chromogenic calixarene, which is slightly acidic in nature due to the presence of the nitro phenol group on the chromogenic moiety, can undergo complexation in the absence of base. This produces the complexed form of the calixarene, which is more acidic than its uncomplexed analogue due to the presence of the positive charge of the metal ion residing in the polar cavity defined by the carbonyl oxygen atoms. In the system investigated, the bases are able to deprotonate the nitrophenol group of the ion–calixarene complex, but not of the uncomplexed calixarene. The nitrophenolate group in the complex may be electrostatically associated with the complexed cation in the form of an internal salt.

^{1}H NMR measurements provided confirmation of complexation. Calix[4]arene tetraesters of the type used in this study undergo several very characteristic changes in proton chemical shifts on complexation with alkali metal cations.[25–29] All three ligands are believed to possess the cone conformation in solution since their immediate precursors, *viz.* acid chlorides **4** and **5**, are known to have this conformation. However, ligand **1** appears to be a distorted cone in solution since the ^{1}H NMR spectrum reveals the presence of two *tert*-butyl signals at 0.84 and 1.33 ppm [Fig. 2(*a*)]. On addition of NaSCN these two signals are replaced by a single resonance at 1.20 ppm, which is indicative of complexation of the cation within a more symmetrical environment defined by the four equivalent ligating arms [Fig. 2(*b*)]. Other changes in the positions of the aromatic protons and the $ArCH_2Ar$ bridging methylene protons upon complexation are consistent with data from other studies with calixarene esters[25] and closely related calix[4]arene nitrophenylazophenol derivatives.[26] These changes confirm that complexation occurs in the absence of base. However, no colour change was observed in these measurements, indicating that complexation without deprotonation was occurring. This lack of colour/spectral change when complexation occurs in the absence of morpholine is indicative of the deprotonation of the nitrophenol being a prerequisite for colour generation. A colour change is observed if a suitable base is available for the uptake of the phenolic proton.

The colour and spectral changes observed upon metal complexation with the monochromogenic ligand **3** suggests that one deprotonation is sufficient for a colorimetric response to be observed, as only one labile proton is available per molecule, in contrast to ligand **1** which has four. The interference studies carried out using fixed concentrations of sodium perchlorate interferent are illustrated in Fig. 3(*a*) and (*b*). From the intercept between the lithium response curve and the sodium interference curve, selectivity coefficients were estimated. Ligand **3** was found to be slightly more selective for lithium than ligand **1**, with selectivity coefficients of 34.7 and 25.1 against 10^{-2} mol dm^{-3} sodium and 14.7 and 11.2 against 10^{-3} mol dm^{-3} sodium, calculated for lithium against sodium for ligand **1** and ligand **3** respectively.

Two Phase Studies.—On introducing a second (aqueous) phase into the system, it is imperative from a sensor point of view that conditions are optimised so that partition coefficients for the base and all forms of the chromogenic calixarene (complexed, complexed and deprotonated, uncomplexed) greatly favour the organic phase, as leaching of the membrane components into the aqueous phase leads to poor sensor response characteristics. A transfer of metal ions from the aqueous to the organic phase is however required. The system involves a number of equilibria with the partition coefficient of the deprotonated complex determining the extent to which the coloured species enters the aqueous phase.

TDDA, which is a more lipophilic base than morpholine, was used in the two phase work in order to maintain the base in the organic phase, thus reducing the tendency of the base to partition out into the aqueous phase and ensuring that the deprotonation of the nitrophenol group would occur in the organic phase. Upon addition of 2.5 cm^3 of water to the system (without metal perchlorates), the formation of a light yellow colour at the interface of the water and the butan-1-ol was observed.

Upon addition of the metal perchlorates to the aqueous phase, an increase in colour intensity was noted in the organic phase at the higher lithium perchlorate concentrations. This colour change was monitored by UV–VIS spectroscopy with an absorbance maximum being noted at 425 nm and an isobestic point at 380 nm [Fig. 4(*a*) and (*b*) for ligands **1** and **3** respectively]. This strongly suggests that the metal perchlorate has been taken up from the aqueous phase and has complexed with the calixarene.

With both ligands **1** and **3**, a transfer of colour due to the complexed ligand into the aqueous phase was noted at lithium and sodium perchlorate concentrations of 10^{-1}–10^{-3} mol dm^{-3}, with the yellow colour diffusing into and throughout the aqueous layer with time. UV–VIS spectra of the yellow aqueous phase gave peaks at 425 nm up to 80% the size of those obtained for the organic layer for ligand **3** and up to 20% for ligand **1**, suggesting that significant leaching of the deprotonated complex into the aqueous phase was occurring. In contrast to calix[4]arene esters which are extremely water insoluble, the movement of colour due to the complexed form of the molecule into the aqueous phase was surprising. The zwitterionic nature of the deprotonated, complexed ligand, is undoubtedly a major factor influencing the transfer of colour from the organic to the aqueous phase, as the deprotonated complex possesses positive charge centred on the metal ion in the cavity, and a negative charge at the deprotonated nitrophenyl chromophore. The variable solubility of these ligands is of some interest, as most calixarenes are very water-insoluble, even when complexed with a cation. Water soluble calixarenes have been synthesised by substitution of carboxyl[30] and sulfonate[31] groups at the *para*-positions. However, with ligands **1** and **3**, it seems that the aqueous solubility can be dramatically altered, *e.g.* by variation of the pH of the aqueous phase. This type of pH or ion dependent solubility raises interesting possibilities for switching ion or ligand transport between phases. As deprotonation of these calixarenes is also a function of the electrochemical environment (the nitrophenol groups can be readily oxidised-reduced, and have well-defined voltammetric behaviour[32]), phase transport could in principle be controlled by means of an externally applied potential.

Table 1

Ligand	[Na$^+$]/mol dm^{-3}	$K_{Li,Na}$
1	10^{-2}	25.1
1	10^{-3}	11.2
2	10^{-2}	43.1
2	10^{-3}	23.2
3	10^{-2}	34.7
3	10^{-3}	14.7

However, for sensor applications involving the immobilisation of the ligand on a fibre optic cable, leaching of the complex into the aqueous phase is undesirable. In order to try and prevent or reduce this effect, a more lipophilic analogue (ligand **2**) bearing C_{18} groups at the *para*-position in place of the *tert*-butyl groups was investigated. The retention of a dichloromethane molecule between two calixarene molecules as suggested by the elemental analysis has been reported by other researchers.[33] Unfortunately, the waxy nature of the product arising from the C_{18} groups precluded the generation of good crystals for confirmation of this molecular arrangement. However, the complexing ability, IR spectra, UV–VIS spectral changes on complexation and lack of aqueous solubility as described below is convincing evidence that the desired compound has been obtained.

From the single phase studies, ligand **2** was also found to be lithium selective. The absorbance spectra [Fig. 1(*c*)], for this compound were very similar to those obtained for the other two ligands, with an absorbance maximum being observed at 425 nm and an isobestic point at 380 nm. Selectivity coefficients for lithium against sodium were obtained as described earlier [Fig. 3(*c*)], with values of 43.1 and 23.2 being obtained for 10^{-2} and 10^{-3} mol dm^{-3} sodium perchlorate respectively. These results indicate that the most lithium selective of the three ligands is ligand **2**.

Ligand **2** also demonstrated the ability to remove metal perchlorates from the aqueous phase as illustrated in Fig. 4(*c*). In contrast to ligands **1** and **3**, no colour transfer from the organic (butan-1-ol) to the aqueous phase was noted even at the higher concentrations. From UV–VIS spectra of the aqueous phase at the three highest lithium perchlorate concentrations, peaks at 425 nm were observed with peak heights less than 5% of the corresponding organic phase peaks. Colour transfer into the aqueous phase was noticed after a few days indicating a

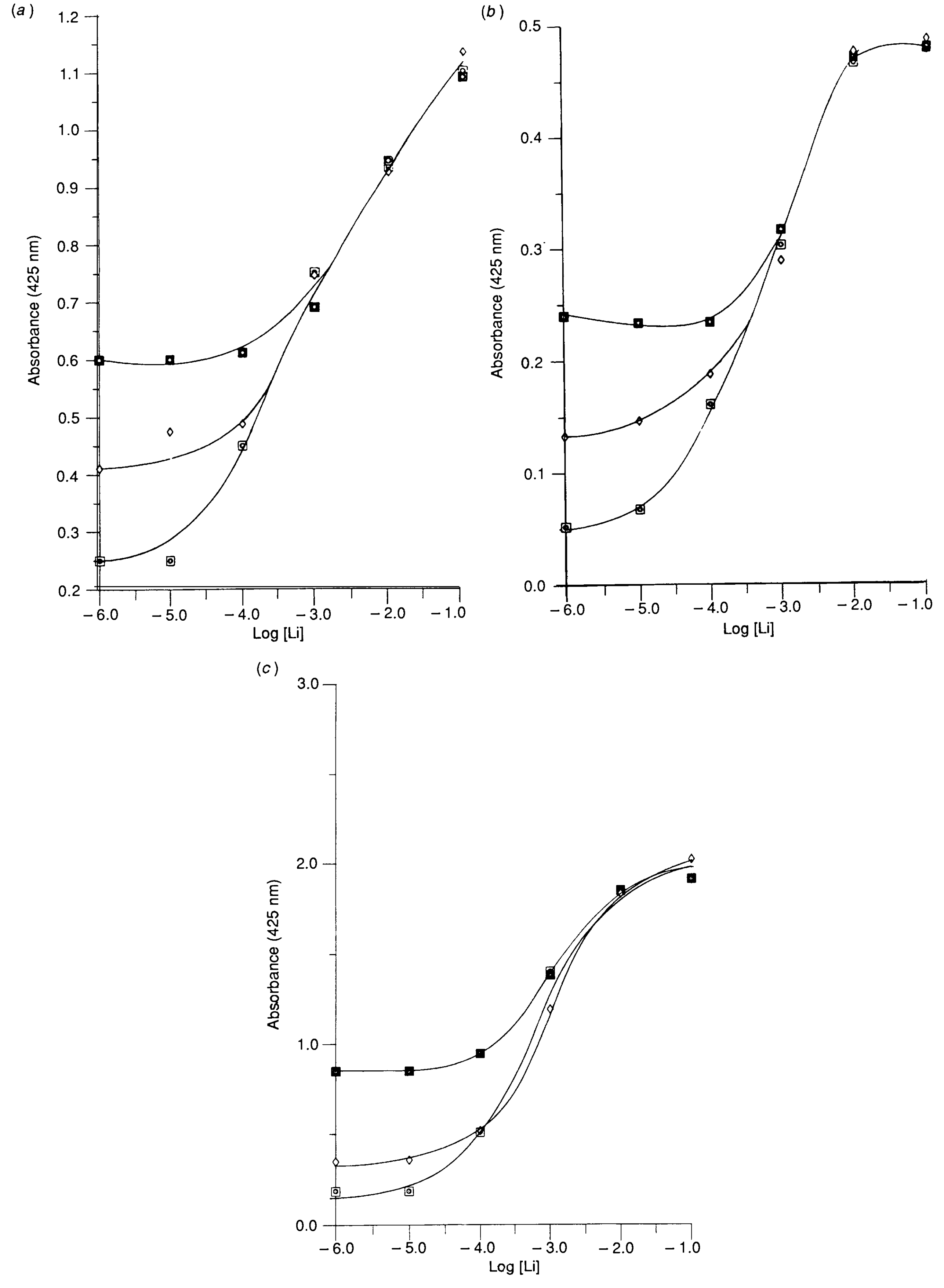

Fig. 3 One-phase studies of the optical response of: (*a*) 5 × 10^{-5} mol dm^{-3} ligand **1** in THF with 20 mm^3 morpholine; (*b*) 10^{-4} mol dm^{-3} ligand **2** in THF with 45 mm^3 morpholine; (*c*) 5 × 10^{-5} mol dm^{-3} ligand **3** in THF with 20 mm^3 morpholine—to additions of Li^+ in the presence of fixed concentrations of sodium perchlorate. From these data, an approximate selectivity coefficient ($K_{Li,Na}$) can be calculated from the concentrations of the ions at the intercept *via* the expression $K_{Li,Na} = C_{Na}/C_{Li}$ (see Table 1).

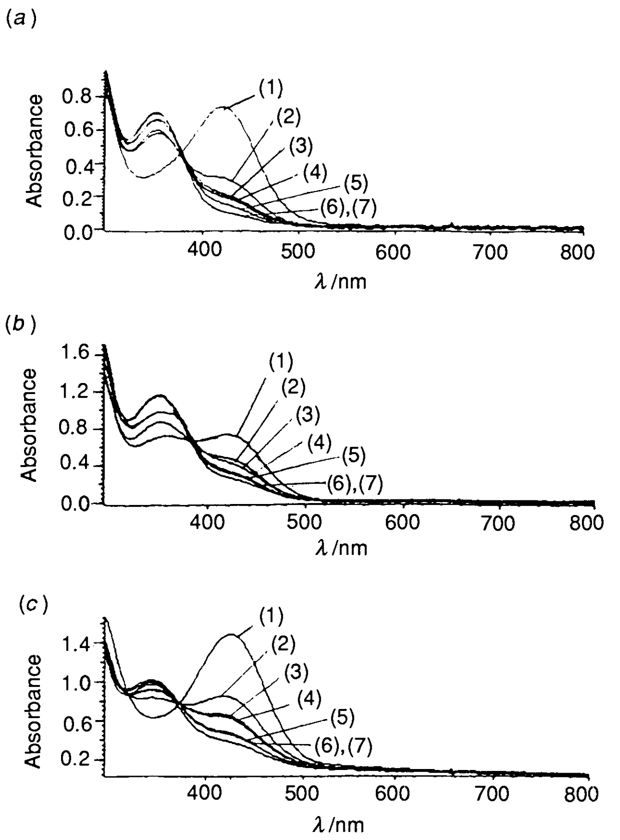

Fig. 4 Two phase studies showing changes in absorbance spectrum of the organic (butan-1-ol) phase for 5×10^{-5} mol dm^{-3} (*a*) ligand **1**, (*b*) ligand **2** and (*c*) ligand **3** with 20 mm^3 of TDDA, when $LiClO_4$ was added to the aqueous phase of the two phase system to give the following aqueous phase concentrations: 0.1 (1), 10^{-2} (2), 10^{-3} (3), 10^{-4} (4), 10^{-5} (5), 10^{-6} (6) and 0 mol dm^{-3} (7)

slow, gradual leaching of the coloured complex from the organic phase.

Conclusions

It has been demonstrated that ligands **1**, **2** and **3** show a chromogenic response to complexation with lithium, and to a lesser extent with sodium. The presence of a base in the system is essential if complexation is to be detected colorimetrically by the deprotonation of a nitrophenol group. All three compounds have been shown to have the ability to extract metals from an aqueous phase and form coloured complexes in butan-1-ol. Leaching of the coloured complex from the organic to the aqueous phase was found to be greatly reduced by the presence of C_{18} groups at the *para*-position. The combination of the optical properties and the presence of these C_{18} groups on the upper rim of the calixarene should also make these materials interesting for Langmuir–Blodgett studies. Work is continuing with these and other chromogenic systems, and with the incorporation of these ligands into fibre optic sensors.

Acknowledgements

We gratefully acknowledge financial support for this research which was jointly funded by the Irish Science and Technology Agency (EOLAS) and Amagruss Electrodes (Ireland) Ltd. (grants no. HEIC/91/327 and SC92/319).

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Paper 3/00484H
Received 26*th January* 1993
Accepted 18*th June* 1993