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New diamino derivatives of *p-tert*-butylcalix[4]arene for oxyanion recognition: synthesis and complexation studies

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We have prepared new diamino derivatives of *p-tert*-butylcalix[4]arene from the reduction of corresponding amide derivatives. The examination of their recognition abilities towards some selected oxyanions shows that the new calix[4]arene amines are mostly more effective receptors than their amide derivatives for dichromate anions and nitrite, and capable of extracting these anions in yields as high as 95%. However, neither the calix[4]arene amines nor their corresponding amides were capable of extracting phosphate or nitrate at pH 1.5.

Keywords: calix[4]arene; diamines; oxyanions; complexation; extraction

Introduction

Calixarenes, well-known macrocyclic molecules with almost unlimited derivatisation potential, possess a unique three-dimensional structure with outstanding shape-recognition possibilities (*1–5*). In the past decade, these compounds have been widely used in supramolecular chemistry as building blocks or molecular scaffolds for the construction of receptors towards ions or neutral molecules (*6–8*). Anion recognition continues to be a very attractive and challenging area of research with the possible application of selective ion receptors in biological and environmental system. Neutral receptors containing units with hydrogen bond donor capability, which can interact with anionic species have become the focus (*9*, *10*).

Although examples of synthetic receptors able to recognise anions were reported since the early stages of supramolecular chemistry, anion recognition chemistry received less attention when compared with cation binding (*9–15*). Recently, various amide/amine-functionalised calixarenes have been reported (*16–23*) as anion receptors, which interact with anions via electrostatic interactions or hydrogen bonding. Our departure point was a report (*22*) on the synthesis and oxyanion recognition abilities of amide and amine derivatives of calix[4]arene. In that work, it was revealed that the protonated calix[4]arene amines were better extractants than were the corresponding amides, although their extraction efficiencies were in low yields. Thus, in the current work we considered that different amine-substituted calix[4]-arenes would be more effective extractants than the previously studied ones for oxyanions. To achieve this aim, we synthesised various calix[4]arene amines from their corresponding amides and examined their extraction abilities towards oxyanions such as dichromate, nitrite, nitrate and phosphate.

Results and discussion

As mentioned above, we prepared a set of new calix[4]arenes and compared their extraction properties for oxyanions with their corresponding amides and the amines previously reported by Roundhill et al. (*22*). We previously developed diamide-derivatised calix[4]arenes (**2**–**4**; Figure 1) with different structures as receptors for dichromate oxyanions (*23*). However, we anticipated that the calix[4]arene-amine derivatives of those calix[4]arene-diamides (Scheme 1) might be more effective ligands for oxyanions than the calix[4]arene-amines that were previously reported (*22*). We have also selected other calix[4]arene amides (**1** and **5**) (*24*, *25*) to see structural effects of the ligands on the extraction. To achieve this goal, first, the calix[4]arene-diamine ligands were synthesised with the reduction of the corresponding diamide derivatives. Here, the treatment of all diamides with the THF–borane complex in dry THF gave the corresponding diamines **6**–**10** in 81, 47, 43, 65 and 72% yields, respectively. The structures of the new calix[4]-arene diamines were identified by spectral and analytical data such as elemental analysis, FT-IR, ^{1}H NMR, ^{13}C NMR and FAB-MS. All reduction reactions were monitored by thin layer chromatography and were checked several times by taking a small sample from the reaction mixture and recording the FT-IR spectrum to monitor the disappearance of the amide carbonyl band

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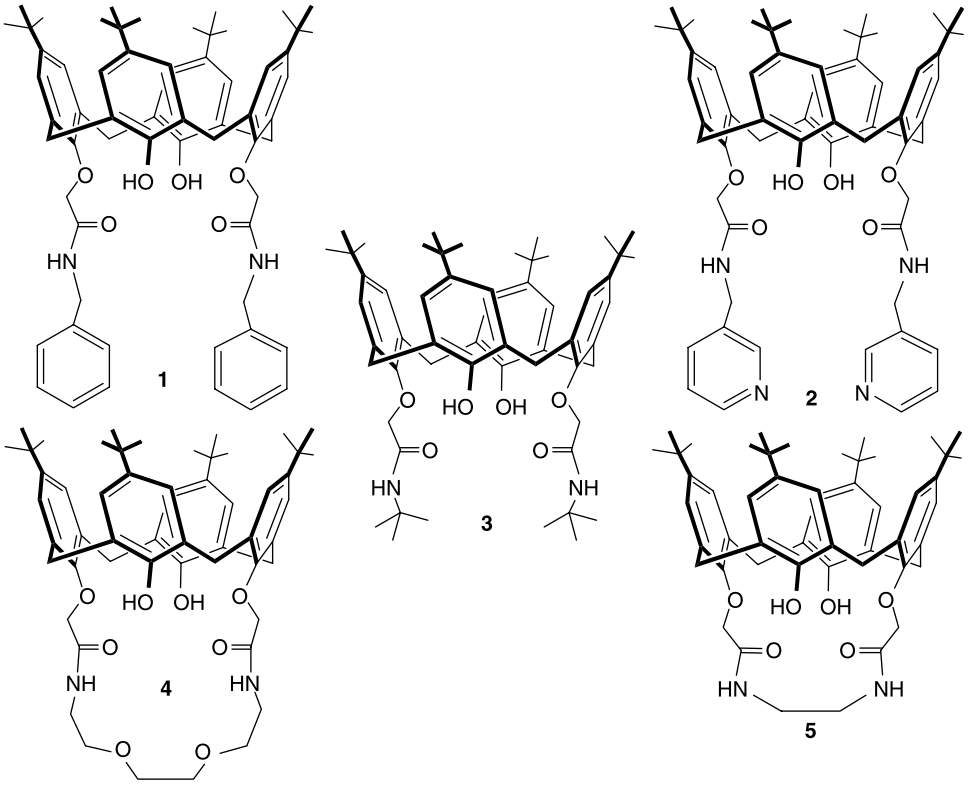


Figure 1. Calix[4]arene amides **1**–**5** (*23*–*25*) synthesised previously.

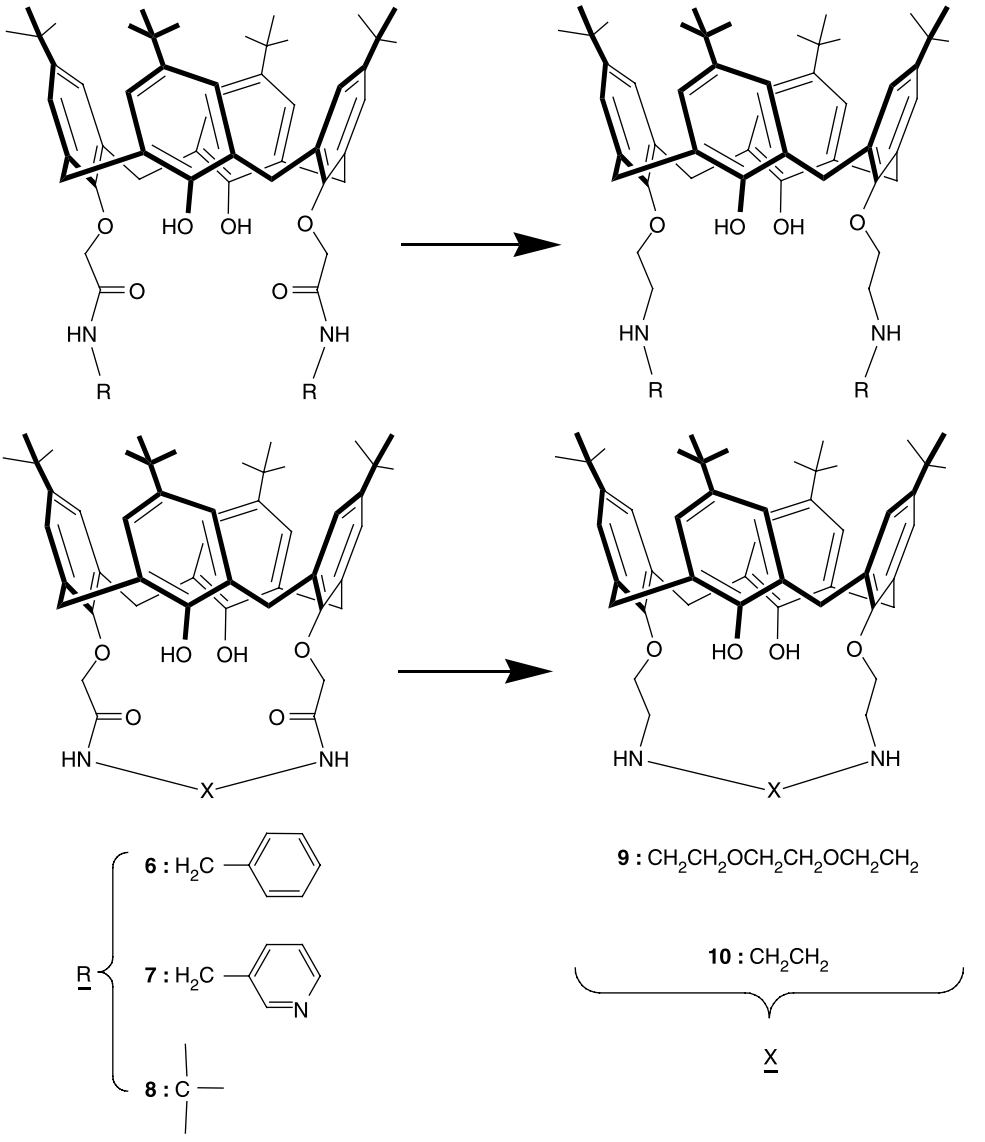
about at 1650 cm^{-1}, and also the simultaneous appearance of a new band belonging to amine groups at about 3200 cm^{-1}.

The FT-IR results showed that the reduction was successful in all cases. After the initial characterisation of new compounds, their ^{1}H NMR and/or ^{13}C NMR spectra were recorded. The spectra of **6**–**10** provided further evidence of successful reduction of the amide functionality, and demonstrated that the compounds were immobilised in the *cone* conformation due to the presence of two pairs of doublets at around 3.30 and 4.20 ppm, indicative of the non-equivalency of the protons of the methylene bridges (ArCH_2Ar) (*1*). However, some of the methylene protons were overlapped in the case of **6** and **7**.

^{1}H NMR spectra of **6** and **7** in $CDCl_3$ showed specific signals such as one triplet ($J = 4.8$ Hz) at 3.07 ppm and broad singlet at 3.28 ppm (OCH_2CH_2NH), one singlet at 3.97 ppm and at 4.11 ppm ($NHCH_2Ar$), the overlapped peaks in the range of 3.39–3.30 ppm and 3.48–3.40 ppm (NH and $ArCH_2Ar$), for **6** and **7**, respectively. Special peaks were observed which proved the evidence of reduction in ^{1}H NMR spectrum of **8**. For instance, one broad singlet for OCH_2CH_2NH protons at 3.14 ppm, one broad singlet for $C(CH_3)_3$—NH protons at 1.25 ppm and one doublet ($J = 9.1$ Hz) at 1.19 ppm for NH protons, were observed. Again, the ^{1}H NMR spectra of cyclic amines **9** and **10** were proof for the complete reduction of amide groups of **4** and **5** due to the disappearance of amide NH protons. Moreover, ^{13}C NMR spectra of all new calix[4]arene amines confirmed the reduction of amide moieties to the corresponding amines.

A preliminary evaluation of the extraction efficiencies of **6**–**10** for chromium(VI) anions was carried out by solvent extraction (*23*) from water into dichloromethane in the pH range of 1.5–4.5. According to the results shown in Figure 2, it has been deduced that all new calix[4]arene-diamine derivatives are very effective ligands for chromium(VI) anions at pH 1.5. This result is not surprising because all ligands contain amine proton-switchable binding moieties, appropriate for the aggregation of anions at low pH (*16*). Importantly, according to the best of our knowledge, the extraction results by **6**–**8** indicate that dichromate anions can be extracted for the first time in this study in quite high yields (90–95%). This can be attributed to the rigid nature of new calix[4]arene amines when they are compared with their previous reported calix[4]arene amine-based anion receptors (*22*).

In light of the above results, we performed extraction studies to investigate the binding capabilities of calix[4]-arene amines towards other oxyanions such as PO_4^{3-}, NO_3^-, NO_2^-, and the results were compared with those of the corresponding calix[4]arene amides. As follows from Table 1, except for **9** (with nitrite), all calix[4]arene amines exhibit higher extractabilities for



Scheme 1. Synthetic route of preparation of calix[4]arene amines **6**–**10**.

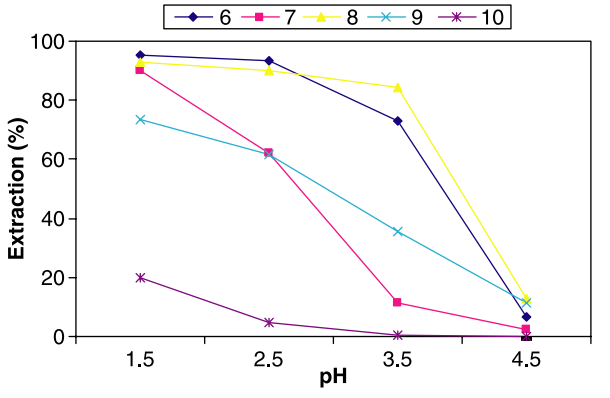


Figure 2. Extraction percentages of dichromate anions by **6**–**10** at different pH values.

both dichromate and nitrite anions than those of amide derivatives, even though the extraction yield is low for **10**. Consequently, it can be postulated that new calix[4]arene amines more strongly complex with dichromates and nitrates than those of their amide analogues, although in case of **9** with nitrite it exceptionally seems reversed.

However, as can be seen from Table 1, there was no evidence of nitrate or phosphate extraction by any of the ligands **1**–**10**. In more acidic solutions, the conversion of phosphate anion into its uncharged form, H_3PO_4, could be a reason for this (*22*); in case of nitrate, it may be ascribed to the structural properties of anion such as size, geometry and conformation. Nevertheless, this result is important in terms of selectivity because it shows that dichromates and nitrites can be extracted over phosphates and nitrates under the current experimental conditions.

Table 1. Extraction percentages[a,b] of oxyanions by calix[4]arene amines and amides at pH 1.5.

Compound	$Cr_2O_7^{2-}$	PO_4^{3-} (H_3PO_4)	NO_3^-	NO_2^-
6 (**1**)	95.3 (<1.0)	<1.0 (<1.0)	<1.0 (<1.0)	76.4 (40.1)
7 (**2**)	90.1 (24.8)[c]	<1.0 (<1.0)	<1.0 (<1.0)	100 (63.3)
8 (**3**)	93.0 (<1.0)[c]	<1.0 (<1.0)	<1.0 (<1.0)	66.3 (35.1)
9 (**4**)	73.6 (64.4)[c]	<1.0 (<1.0)	<1.0 (<1.0)	74.5 (99.0)
10 (**5**)	20.1 (<1.0)	<1.0 (<1.0)	<1.0 (<1.0)	98.8 (41.2)

[a] Averages and SDs (±0.5) calculated for data obtained from three independent extraction experiments.
[b] Aqueous phase, [anion salt] = 1.0×10^{-4} M; organic phase, dichloromethane, [ligand] = 1.0×10^{-3} M at 25°C, for 1 h.
[c] Ref. (*23*).

Interestingly, no binding is observed by some calix[4]arene amides **1**, **3**, **5** for dichromates; however, the others **2** and **4** exhibit a noteworthy extractability (24.8 and 64.4%, respectively). On the other hand, all of them furnish complexes with nitrite anion in high yields.

The extraction with cyclic amide receptor **4** is very efficient for nitrite (99%); however, it is quite less (41.2%) than that observed with the other cyclic amide receptor **5**. This may be due to the smaller ring size of **5** when compared with that of **4**. It is noted that the rigidification of receptor by bridging with its oxa-amino moieties leads to the stable and facile preorganisation between the calix[4]arene arms and anions. However, after the extraction of nitrite by their corresponding cyclic calix[4]arene amines **9** and **10**, the extractability order is reversed and the extraction yield with **10** (98.8%) is higher than with **9** (74.5%).

Among the calix[4]arene amines, **6**–**8** are the most effective receptors for dichromates with yields between 90 and 95%; however, only **7** and **10** are excellent receptors for nitrites in 100 and 98.8% yields, respectively. On the other hand, in case of calix[4]arene amides, only **4** is an excellent extractant for both dichromates (64.4%) and nitrites (99%).

To gain a deeper insight into the complexation process, all extraction data were analysed by using classical slope analysis method. Assuming the extraction of an anion (A) by the anion receptor (L) according to the following equilibrium

$$n(\mathrm{L})_{org} + n(\mathrm{A})_{aq} \rightleftharpoons ((\mathrm{L})_n, (\mathrm{A})_n)_{org}. \quad (1)$$

The extraction constant K_{ex} is then defined by

$$K_{ex} = \frac{[((\mathrm{L})_n, (\mathrm{A})_n)]_{org}}{[\mathrm{A}]^n_{aq}[\mathrm{L}]^n_{org}}. \quad (2)$$

Equation (2) can be re-written as

$$\log D_A = \log K_{ex} + n \log[L]_{org}, \quad (3)$$

where D_A is defined as the ratio of the analytical concentration of the anion (A) in both phases:

$$D_A = [\mathrm{A}]_{org}/[\mathrm{A}]_{aq}. \quad (4)$$

Consequently, a plot of log D_A vs. log [*L*] may lead to a straight line whose slope allows us to access the stoichiometry of the extracted species. Figure 3 represents the extractions into dichloromethane at different concentrations of **6**–**10** for dichromate. A linear relationship between log *D* vs. log [*L*] is observed with a slope for dichromate by **6**–**10**, which equals 1.28, 0.99, 1.18, 1.23 and 1.25 at pH 1.5, respectively, suggesting that **6**–**10** form 1:1 complexes with dichromate anions (Figure 4).

However, it is well known that at more acidic conditions $Na_2Cr_2O_7$ is converted into $H_2Cr_2O_7$, and after ionisation in an aqueous solution it exists in the $HCr_2O_7^-/Cr_2O_7^{2-}$ form (*16*). This allowed us to consider these simultaneous extractions of 1:1 complexes according to the following equilibria (Scheme 2).

According to these assumptions, the extraction constants (K_{ex}) have been calculated from the experimental data. Calculations of these constant values lead to log K_{ex} (±0.2) = 5.12, 4.10, 4.31, 3.67, 1.95 for **6**–**10**, respectively.

Moreover, we also performed the study of classical slope analysis for both nitrite and dichromate anions with **6** to clarify the unity between nitrite and dichromate anion

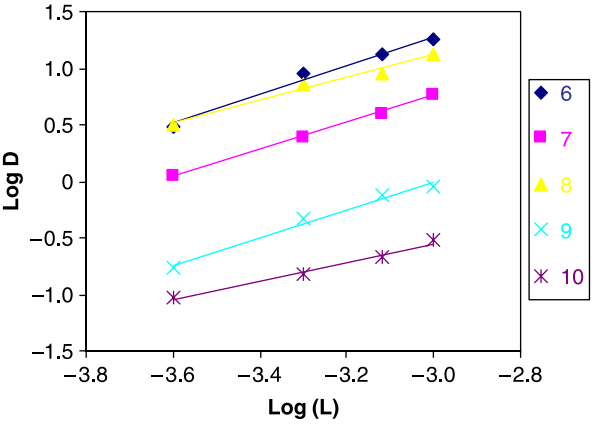


Figure 3. Log *D* vs. log [*L*] for the extraction of dichromate and its anions by the ligands **6**–**10** from an aqueous phase into dichloromethane at 25°C and pH 1.5.

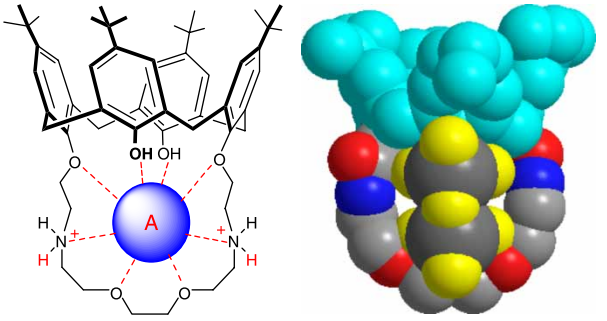


Figure 4. The proposed interactions of compound **9** with dichromate and its anions (A : $H_2Cr_2O_7/HCr_2O_7^-/Cr_2O_7^{2-}$) at pH 1.5 and side view of one molecular bowl of **9.A** using space-filling representation (hydrogen atoms are omitted for clarity).

$$LH^+ / LH_2^{2+} / L_pH_3^{3+} / L_p H_4^{4+}{}_{(org)} + H_2 Cr_2O_7/HCr_2O_7^-/Cr_2O_7^{2-}{}_{(aq)}$$

$$\rightleftharpoons$$

$$\left[LH^+ / LH_2^{2+} / L_pH_3^{3+} / L_p H_4^{4+}, (H_2 Cr_2O_7/HCr_2O_7^-/Cr_2O_7^{2-})\right]_{(org)}$$

$$L = 6 - 10;\ L_p = 7$$

Scheme 2. Suggested extraction mechanism of dichromate and its anions by **6**–**10** at pH 1.5.

complexation behaviour at pH 1.5. The results revealed that dichromate anions complexed in a 1:1 stochiometry, while nitrite was extracted by **6** in a 1:2 ratio. These results probably implied that the structural similarities of both the anions were a designative factor for selectivity over other anions. Figure 5 represents this complexation phenomenon of both the anions with **6**.

The binding properties of **6** towards dichromate anions have also been investigated by the ^{1}H NMR technique. Unfortunately, the region of NH signals became partly invisible and/or broadened upon addition of the anion.

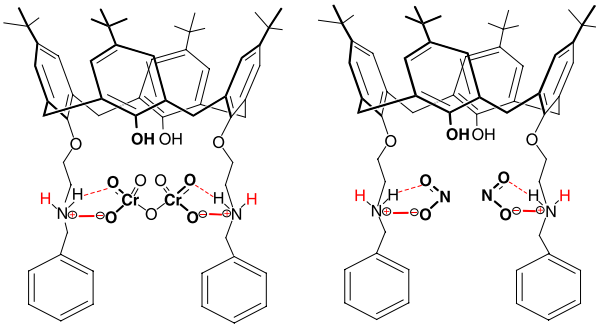


Figure 5. The suggested complexation phenomena with dichromate and nitrite anions with **6** at pH 1.5.

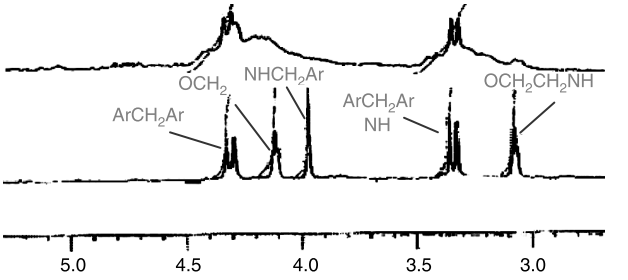


Figure 6. ^{1}H NMR spectra of complexed (above) and uncomplexed (below) **6** with dichromate.

Nevertheless, ^{1}H NMR spectra of complexed and uncomplexed **6** (Figure 6) with dichromate anion are an evidence that the complexation process takes place through NH and NH-bonded moieties of **6**.

Conclusion

In conclusion, new calix[4]arene diamine derivatives were synthesised and their extraction behaviour were evaluated by solvent extraction for some selected oxyanions. The results showed that the extraction of dichromate and nitrite anions by diamine-derivatised calix[4]arenes mostly took place in quite high yields and was greater than their corresponding amide analogues, while it is negligible for phosphate and nitrate.

Experimental

General

Melting points were determined using an Electrothermal 9100 apparatus in a sealed capillary and were uncorrected. ^{1}H NMR spectra were recorded on a Bruker 400 MHz spectrometer in $CDCl_3$ with TMS as the internal standard. IR spectra were obtained on a Perkin-Elmer 1605 FT-IR spectrometer using KBr pellets. UV–visible spectra were obtained on a Shimadzu 160A UV–visible spectrophotometer. Elemental analyses were performed using a Leco CHNS-932 analyser. FAB-MS spectra were taken on a Varian MAT 312 spectrometer. An Orion 420A + pH meter was used for the pH measurements. Analytical TLC was performed using Merck prepared plates (silica gel 60 F254 on aluminium). Flash chromatography separations were performed on a Merck Silica Gel 60 (230–400 mesh). All reactions, unless otherwise noted, were conducted under nitrogen atmosphere. All starting materials and reagents used were of standard analytical grade from Fluka, Merck and Aldrich, and used without further purification. Toluene was distilled from CaH_2 and stored over sodium wire. Other commercial grade solvents were distilled and stored over molecular sieves. Anions were used as their sodium salts. The drying agent employed was

anhydrous $MgSO_4$. All aqueous solutions were prepared with deionised water that had been passed through a Millipore milli-Q Plus water purification system.

General procedure for the reduction of calix[4]arene-based diamides to diamines 6–10

The reduction reactions were performed by adapting according to literature procedure (*22*). Compound **6**: yield 81%; mp 130°C; ^{1}H NMR δ 7.42 (d, 4H, $J = 7.4$ Hz, Bnz-H-*o*), 7.31 (t, 4H, $J = 7.3$ Hz, Bnz-H-*m*), 7.26–7.23 (overlapped, 4H, OH and Bnz-H-*p*), 7.05 (s, 4H, ArH-calix), 6.87 (s, 4H, ArH-calix), 4.31 (d, 4H, $J = 13.0$ Hz, $ArCH_2Ar$), 4.11 (t, 4H, $J = 4.8$ Hz, OCH_2), 3.97 (s, 4H, NH—CH_2—Ar), 3.39–3.30 (overlapped, 6H, NH and $ArCH_2Ar$), 3.07 (t, 4H, $J = 4.8$ Hz, OCH_2CH_2NH), 1.27 (s, 18H, *tert*-butyl), 1.02 (s, 18H, *tert*-butyl); ^{13}C NMR δ 150.3, 149.6, 147.3, 141.9, 132.9, 128.4, 128.3, 127.8, 126.9, 125.7, 125.3 (Ar-C), 77.0 (OCH_2), 53.4 ($NHCH_2$-Ar), 48.6 (OCH_2CH_2NH), 34.0, 33.8, 32.0, 31.7 ($C(CH_3)_3$), 31.1 ($ArCH_2Ar$); IR (KBr) 3180 cm^{-1} (NH); MS-FAB *m*/*z* 915.3 [$(M - Na)^+$, calcd 938.5]. Anal. calcd for $C_{62}H_{78}N_2O_4$: C, 81.36; H, 8.59; N, 3.06. Found: C, 81.51; H, 8.65; N, 2.99. Compound **7**: yield 47%; mp 105°C; ^{1}H NMR δ 8.71 (brs, 2H, Py-H), 8.55 (brs, 2H, Py-H), 8.02 (d, 2H, $J = 7.9$ Hz, Py-H), 7.35 (t, 2H, $J = 6.5$ Hz, Py-H), 7.25 (s, 2H, OH), 7.08 (s, 4H, ArH), 6.99 (s, 4H, ArH), 4.26–4.14 (overlapped, 8H, $ArCH_2Ar$ and OCH_2), 4.11 (s, 4H, NH—CH_2—Ar), 3.48–3.40 (overlapped, 4H, NH and $ArCH_2Ar$), 3.28 (brs, 4H, OCH_2CH_2NH), 1.22 (s, 18H, *tert*-butyl), 1.18 (s, 18H, *tert*-butyl); ^{13}C NMR δ 150.1, 149.4, 147.2, 141.8, 132.7, 128.3, 128.2, 127.9, 126.7, 125.2 (Ar-C), 77.1 (OCH_2), 53.3 ($NHCH_2Ar$), 47.9 (OCH_2CH_2NH), 34.0, 33.7, 32.1, 31.7 ($C(CH_3)_3$), 31.0 ($ArCH_2Ar$); IR (KBr) 3176 cm^{-1} (NH); MS-FAB *m*/*z* 917.3 [$(M - Na)^+$, calcd 940.6]. Anal. calcd for $C_{60}H_{76}N_4O_4$: C, 78.56; H, 8.35; N, 6.11. Found: C, 78.71; H, 8.27; N, 6.17. Compound **8**: yield 43%; mp 256°C; ^{1}H NMR δ 7.26 (s, 2H, OH), 7.06 (s, 4H, ArH), 6.76 (s, 4H, ArH), 4.27 (d, 4H, $J = 12.3$ Hz, $ArCH_2Ar$), 4.16 (brs, 4H, OCH_2), 3.33 (d, 4H, $J = 13.2$ Hz, $ArCH_2Ar$), 3.14 (brs, 4H, OCH_2CH_2NH), 1.30 (s, 18H, *tert*-butyl-Ar), 1.25 (brs, 18H, *tert*-butyl-NH), 1.19 (d, 2H, $J = 9.1$ Hz, NH), 0.92 (s, 18H, *tert*-butyl-Ar); ^{13}C NMR δ 150.5, 149.6, 147.0, 141.9, 141.8, 132.4, 128.2, 128.0, 125.8, 125.5, 125.1 (Ar-C and NH—C), 77.0 (OCH_2), 42.5 (OCH_2CH_2NH), 33.9, 33.8, 33.0, 32.4, 31.8, 31.7, 31.5, 31.2, 31.0 (Ar-$C(CH_3)_3$ and NH—$C(CH_3)_3$), 28.9 ($ArCH_2Ar$); IR (KBr) 3151 cm^{-1} (NH); MS-FAB *m*/*z* 847.3 [$(M - Na)^+$, calcd 870.7]. Anal. calcd for $C_{56}H_{82}N_2O_4$: C, 79.38; H, 9.75; N, 3.31. Found: C, 79.62; H, 9.61; N, 3.42. Compound **9**: yield 65%; mp 145°C; ^{1}H NMR δ 7.13–6.97 (overlapped, 6H, ArH and OH), 6.71 (brs, 2H, ArH), 6.66 (brs, 2H, ArH), 4.41 (t, 2H, $J = 9.4$ Hz, $ArOCH_2$), 4.32–4.04 (overlapped, 10H, $ArOCH_2$, OCH_2CH_2O and $ArCH_2Ar$), 3.89 (brd, 2H, $J = 9.4$ Hz, $ArOCH_2CH_2NH$), 3.69 (brs, 1H, $ArOCH_2CH_2NH$), 3.64 (d, 2H, $J = 9.2$ Hz, $NHCH_2$-CH_2O), 3.53 (d, 2H, $J = 9.3$ Hz, $NHCH_2CH_2O$), 3.42 (t, 1H, $J = 11.2$ Hz, $NHCH_2CH_2O$), 3.38–3.25 (overlapped, 6H, $ArCH_2Ar$ and NH), 3.21 (brt, 2H, $J = 6.4$ Hz, $NHCH_2CH_2O$), 3.10 (brs, 1H, $ArOCH_2CH_2NH$), 2.85 (t, 1H, $J = 10.7$ Hz, $NHCH_2CH_2O$), 1.31 (s, 18H, *tert*-butyl), 0.86 (s, 18H, *tert*-butyl); ^{13}C NMR δ 151.3, 149.8, 147.1, 141.9, 132.7, 128.8, 128.4, 125.9, 125.7, 125.4 (Ar-C), 75.8 (OCH_2), 55.2 ($NHCH_2CH_2$), 48.9 (OCH_2CH_2NH), 34.1, 33.6, 32.3, 31.8 ($C(CH_3)_3$), 31.0 ($ArCH_2Ar$); IR (KBr) 3218 cm^{-1} (NH); MS-FAB *m*/*z* 849.2 [$(M - Na)^+$, calcd 872.8]. Anal. calcd for $C_{54}H_{76}N_2O_6$: C, 76.37; H, 9.02; N, 3.30. Found: C, 76.51; H, 8.95; N, 3.40. Compound **10**: yield 72%; mp 253°C; ^{1}H NMR δ 7.07 (d, 4H, $J = 9.6$ Hz, ArH), 6.98 (d, 4H, $J = 8.6$ Hz, ArH), 6.93 (s, 2H, OH), 4.42 (d, 2H, $J = 4.4$ Hz, OCH_2), 4.24–3.93 (overlapped, 7H, OCH_2, $ArCH_2Ar$ and CH_2NH), 3.63 (t, 1H, $J = 11.8$ Hz, $NHCH_2CH_2NH$), 3.55–3.27 (overlapped, 8H, OCH_2CH_2NH, $ArCH_2$-Ar and NH), 3.25 (brd, 2H, $J = 10.6$ Hz, $NHCH_2CH_2NH$), 3.08 (brs, 1H, OCH_2CH_2NH), 2.94 (t, 1H, $J = 11.5$ Hz, 1.22 (s, 18H, *tert*-butyl), 1.15 (s, 18H, *tert*-butyl); ^{13}C NMR δ 150.4, 150.1, 147.2, 141.5, 132.5, 128.4, 127.9, 125.7, 125.4, 125.0 (Ar-C), 72.3 ($ArOCH_2$), 67.1 (OCH_2CH_2O), 55.9 ($NHCH_2CH_2O$), 49.1 (OCH_2CH_2NH), 34.2, 33.8, 32.7, 31.9 ($C(CH_3)_3$), 31.1 ($ArCH_2Ar$); IR (KBr) 3193 cm^{-1} (NH); MS-FAB *m*/*z* 761.1 [$(M - Na)^+$, calcd 784.6]. Anal. calcd for $C_{50}H_{68}N_2O_4$: C, 78.90; H, 9.00; N, 3.68. Found: C, 79.11; H, 9.05; N, 3.75.

Complexation studies

The anion extraction experiments of *p*-*tert*-butylcalix[4]-arene diamine derivatives **6**–**10** were performed following Pedersen's procedure (*26*). An aqueous solution of sodium salt of anion (10 ml of a 1×10^{-4} M; 0.01 M KOH/HCl solution was used in order to obtain the desired pH at equilibrium) and calixarene ligand (10 ml of 1×10^{-3} M) in CH_2Cl_2 were shaken vigorously in a stoppered glass tube with a mechanical shaker for 2 min and then magnetically stirred in a thermostated water bath at 25°C for 1 h, and finally left standing for an additional 30 min. The concentration of anion remaining in the aqueous phase was then determined as described previously (*23*) for dichromate anions or colorimetrically for nitrite, nitrate and phosphate anions using a spectrophotometer and suitable reagents were supplied by Hach Lange Company, Dublin, Ireland. Blank experiments showed that no dichromate extraction occurred in the absence of calix[4]arene amine derivatives. The percent extraction (*E*%) was calculated from the absorbance *A* of the aqueous phase measured at 346 nm (for pH 1.5–4.5) using the following expression:

$$E\% = [(A_0 - A/A_0)] \times 100, \quad (5)$$

where A_0 and A are the initial and final concentrations of the dichromate ion before and after the extraction, respectively.

In ^{1}H NMR complexation studies, the chloroform solution (10^{-3} M) of **6** was treated at room temperature with an excess of chromium(VI) anions salts for 72 h. After filtration, the solvent was evaporated to dryness under vacuum. The resulting solid was dissolved in $CDCl_3$ and ^{1}H NMR spectra were taken.

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