Calix[4]arenes with CMPO functions at the narrow rim. Synthesis and extraction properties

Silvia Barboso,[a] Alejandro Garcia Carrera,[b] Susan E. Matthews,[c] Françoise Arnaud-Neu,[a] Volker Böhmer,*[c] Jean- François Dozol,[b] Hélène Rouquette[b] and Marie-José Schwing-Weill[a]

[a] *ECPM, Laboratoire de Chimie-Physique, UMR 7512 au CNRS, 25, rue Becquerel, F-67087 Strasbourg Cedex 2, France*
[b] *CEA Cadarache, DCC/DESD/SEP/LPTE, F-13108 St. Paul lez Durance, France*
[c] *Fachbereich Chemie und Pharmazie, Abteilung Lehramt Chemie, Johannes-Gutenberg-Universität, Duesbergweg 10-14, D-55099 Mainz, Germany*

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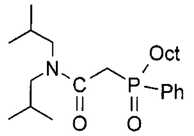
The synthesis of three new derivatives of *tert*-butylcalix[4]arene bearing four carbamoylmethylphosphine oxide (CMPO) groups as ligating functions on the narrow rim is described. These are easily prepared in 65–80% yield *via* acylation of the corresponding fixed cone aminoalkoxy (C_2 to C_4) derivatives with *p*-nitrophenyl (diphenylphosphoryl)acetate. Extraction studies of selected lanthanides (La^{3+}, Eu^{3+}, Yb^{3+}) and thorium (Th^{4+}) from 1 M HNO_3 to CH_2Cl_2 show a strong increase of the percentage extracted (%*E*) with increasing length of the spacer. Extraction of Am^{3+}, La^{3+}, Nd^{3+}, Sm^{3+} and Eu^{3+} from (0.1–4) M HNO_3 into *o*-nitrophenyl hexyl ether shows, in contrast to the wide rim CMPO derivative, no decrease of the distribution coefficient for higher concentrations of nitric acid.

Introduction

Nuclear fuel reprocessing is important to reduce the toxicity and volume of waste for disposal. Plutonium and uranium are effectively removed from the waste stream using the PUREX[1] process. Following this treatment, the waste contains numerous long-lived radionuclides. These can be subdivided into the β and γ emitters (Tc, Cs, I) and the α-emitters (the transplutonium actinides). Selective extraction of these latter compounds and their subsequent transmutation into short lived or non-radioactive radionuclides is a vital process in the management of waste.

Liquid–liquid extraction and de-categorisation of liquid waste is currently achieved industrially by the TRUEX process.[2] This utilises CMPO **1** [(*N*,*N*-diisobutylcarbamoylmethyl)octylphenylphosphine oxide] as the extractant. Both the C=O and P=O groups act as ligating functions and the extracted complex contains three molecules of **1** per cation.[3] Although **1** is a powerful extractant, it shows little discrimination between actinides and lanthanides. Actinides are a minority but more toxic constituent of nuclear waste in comparison to lanthanides. Ideally extractants are required with high actinide/lanthanide selectivity. Pre-organisation of a number of CMPO ligating groups onto a molecular platform could both enhance the extraction efficiency due to chelate effects and increase its selectivity through their specific geometrical arrangement.

Calixarenes[4] are readily available macrocycles on which ligating groups can be assembled in well defined mutual arrangement. A large number of cation extractants based on calixarenes have been developed in which this pre-organisation has been shown to favour specificity of extraction.[5] In most cases ligating functions have been attached to the narrow (lower) rim *via* ether linkages. Recently we have prepared a number of calix[4]- and -[5]arenes incorporating CMPO analogous functions (NH–C(O)–CH_2–P(O)–Ph_2) on the wide (upper) rim,[6] an idea which was subsequently taken up by Reinhoudt *et al.*[7] with structurally analogous, but more rigid, cavitands derived from resorcarenes.[8] These wide rim substituted calix[4]arenes **2** are not only more powerful extractants than **1** but also have a pronounced selectivity for actinides and lighter lanthanides.[9]



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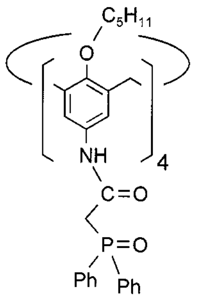

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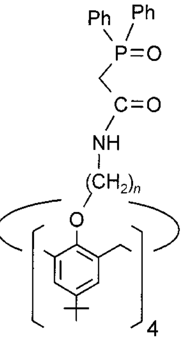

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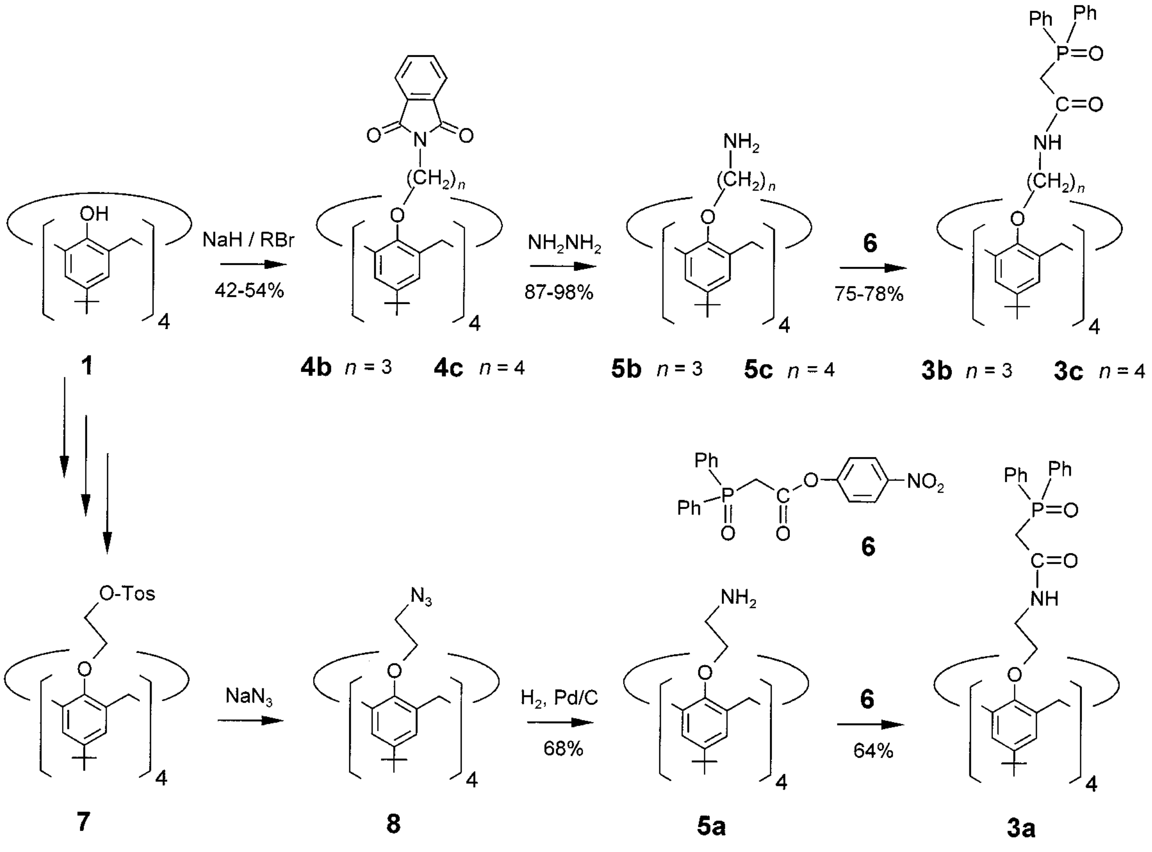
In order to investigate further the effects of pre-organisation on extraction efficiency and selectivity, narrow rim CMPO substituted calix[4]arenes **3** were envisaged as an alternative. We report here the synthesis and first extraction studies of this new class of extractants.

Results and discussion

Syntheses

The calixarene based CMPO-ligands **3b** and **3c** were prepared in three steps from *p-tert*-butylcalix[4]arene. Alkylation with *N*-(3-bromopropyl)phthalimide in the presence of NaH gave the desired peralkylated product **4b** in the cone conformation after chromatographic separation. Treatment with hydrazine in ethanol enabled the removal of the phthalimide protecting



Scheme 1

groups thus revealing a primary amine **5b** suitable for further acylation. Acylation with *p*-nitrophenyl (diphenylphosphoryl)acetate **6**[6] in toluene gave **3b** in 75% yield. Compound **3c** was prepared in an analogous manner starting with alkylation by *N*-(4-bromobutyl)phthalimide. This offers easier access to the tetraamine **5c**, previously obtained by reduction of the corresponding tetranitrile.[10]

Some synthetic difficulties were encountered in the preparation of **3a**. Alkylation with *N*-(2-bromoethyl)phthalimide was unsuccessful under a range of conditions (NaH–DMF, K_2CO_3–MeCN, RT/heat). Isolation of *N*-ethenylphthalimide from the reaction mixture suggested that elimination of the alkylating agent occurs rather than substitution.

In a second approach, bromoacetonitrile was evaluated as an alkylating agent, as subsequent reduction with a complex hydride would yield the desired amine. Once again the desired per alkylated product could not be prepared from *p-tert*-butylcalix[4]arene under a wide range of reaction conditions. Attempts to further alkylate the known 1,3-diether[11] under extreme conditions (NaH–DMF, 75 °C)[10] resulted in an 80:20 mixture (established from NMR integration) of tri- and tetra-alkylated material which could neither be separated by crystallisation nor chromatography.

However, **3a** can be prepared in three steps from the known calixarene derivative **7**.[10] The tosyl derivative undergoes nucleophilic substitution by azide on treatment with NaN_3 in DMF thus introducing nitrogen functionality. The resulting azide **8** is not isolated but immediately catalytically reduced (H_2/Pd/C) to the amine **5a**. Subsequent acylation gives the desired narrow rim CMPO substituted calix[4]arene **3a**. Scheme 1 summarises these synthetic pathways and the yields obtained.

Extraction of lanthanides(III) and thorium(IV) by dichloromethane

To obtain a first insight into the extraction properties of these novel ligands, the extraction of a number of non-radioactive elements was investigated. The results of the extraction of Th^{4+} and the lanthanides La^{3+}, Eu^{3+} and Yb^{3+} ($c_M = 10^{-4}$ M) from a 1 M nitric acid solution into dichloromethane are shown in Table 1 and illustrated in Fig. 1 for the three ligands **3a–c**. For comparative purposes the wide rim CMPO calixarene **2** is also included.

Table 1 Extraction percentage (%*E*)[a] of lanthanide and thorium nitrates by ligands **3a–c** and **2** from 1 M HNO_3 aqueous solution into dichloromethane ($T = 20$ °C)

Cations	c_L	**3a**	**3b**	**3c**	**2**
Th^{4+}	10^{-4}	76 ± 1	81 ± 2	96 ± 1	61 ± 1
La^{3+}	10^{-3}	19 ± 1	13 ± 2	70 ± 3	98 ± 1
	5×10^{-3}		62 ± 3		
Eu^{3+}	10^{-3}	16 ± 1	12.5 ± 0.8	68 ± 1	58 ± 1
	5×10^{-3}	63 ± 3[c]	59 ± 1	94[b]	
Yb^{3+}	10^{-3}	2.6 ± 0.7	≤2	37 ± 2	3 ± 2
	5×10^{-3}		22 ± 1		

[a] Mean values of a minimum of four different experiments, the precision corresponds to $\pm\sigma_{n-1}$, σ_{n-1} being the standard deviation on the mean. [b] Extrapolated from the log–log plots. [c] A little precipitation between the two phases.

Compounds **3a–c** are all highly efficient extractants of thorium, more efficient even than **2**, having extraction values between 80 and nearly 100% when applied at a concentration as low as 10^{-4} M. In contrast acceptable extraction values for the lanthanides are only achieved at higher ligand concentrations ($c_L = 10^{-3}$ M). Thus **2** and **3a–c** can be considered to be selective extractants of thorium over lanthanides. The selectivity of extraction observed for the wide rim CMPO calixarene **2** is considerably enhanced in the narrow rim CMPO calixarenes **3a–c**. The most selective extractant for Th^{4+}/Eu^{3+} and Th^{4+}/La^{3+} is **3b**, which is slightly better than **3a**, whereas **3c** is the least selective.

It can thus be proposed that extraction of a particular cation depends both on the size of the cavity and on the flexibility of the ligands, for example the more flexible **3c** is a more efficient

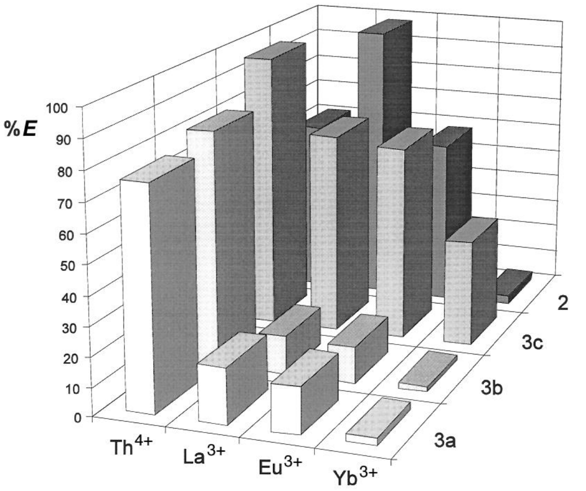


Fig. 1 Extraction (%*E*) of thorium(IV) and lanthanides(III) by calixarenes **2** and **3**. Aqueous phase: cation nitrate $c_M = 10^{-4}$ M in 1 M HNO_3, organic phase: $c_L = 10^{-4}$ M for thorium and 10^{-3} M for the lanthanides.

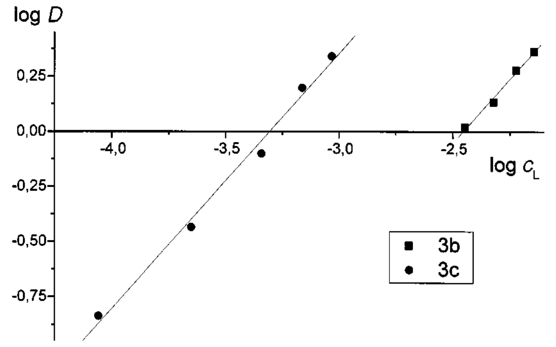


Fig. 2 Plots of log *D* *versus* log c_L for the extraction of europium nitrate ($c_M = 10^{-4}$ M) by **3b** and **3c** from an aqueous phase (1 M HNO_3) into dichloromethane at 20 °C. (Slope **3b** = 1.164, **3c** = 1.156.)

extractant of all cations studied despite the rather large cavity. This is most pronounced for Yb^{3+} which is only weakly extracted by **2** and **3a**,**b** but extracted well by **3c**. As this is a heavy lanthanide it has a considerably smaller cationic radius than La^{3+} or Eu^{3+} and would be expected to be complexed best by ligands with a small cavity. However it seems that the more flexible **3c** is able to form a cavity of the appropriate size more easily than **2** or **3a**,**b**.

With ligand **2**, the extraction level strongly decreases along the series, from lanthanum to europium and to ytterbium.[9] With the three narrow rim CMPO calixarenes, there is also a decrease of extraction along the series but this trend is much less pronounced than for **2**. %*E* values for europium are only slightly lower than for lanthanum and also the further decrease of %*E* from europium to ytterbium is less important than for **2**.

For **3b** and **3c** the extraction of europium was studied as a function of the ligand concentration c_L. Plots of log *D* (where $D = \%E/(100 - \%E)$ is the distribution coefficient) *versus* log c_L are linear (Fig. 2) with a slope close to 1 suggesting that the cation may be extracted as a 1 : 1 complex. Analogous studies with wide rim CMPOs similar to **2** formerly resulted in a slope of 2.[6]

Extraction of lanthanides and americium(III) with *o*-nitrophenyl hexyl ether

Extraction of americium and lanthanides was also investigated with *o*-nitrophenyl hexyl ether (NPHE) as the organic phase at varying concentrations of nitric acid. The results for the extraction of Am^{3+} and the lanthanides La^{3+}, Nd^{3+}, Sm^{3+} and Eu^{3+} ($c_M = 10^{-5}$ M) by the ligands **2** and **3** from a 3 M nitric acid solution into NPHE are shown in Fig. 3. Under these conditions **3a**–**c** are somewhat less efficient extractants of all the cations examined than **2**. Interestingly, however, the extraction efficiencies of calixarenes **3** increase at higher acidities unlike **2**, which shows a maximum at pH = 1.5–2 (Fig. 4).

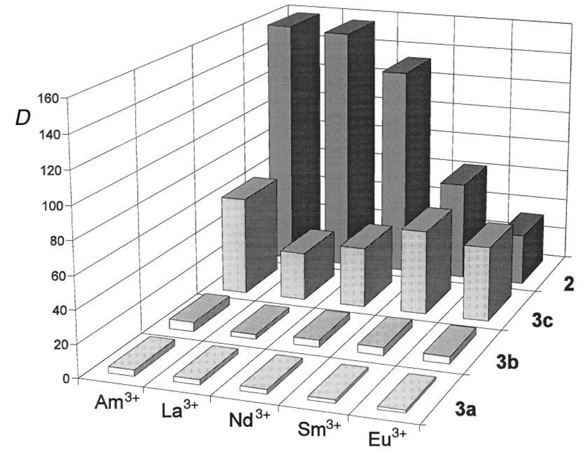


Fig. 3 Distribution coefficients (*D*) of americium, lanthanum, neodymium, samarium and europium for the calixarenes **2** and **3**. Aqueous phase: 3 M HNO_3, $c_{Ln} = 10^{-5}$ M, $c_{Am} = 10^{-9}$ M, organic phase: $c_L = 10^{-3}$ M in *o*-nitrophenyl hexyl ether.

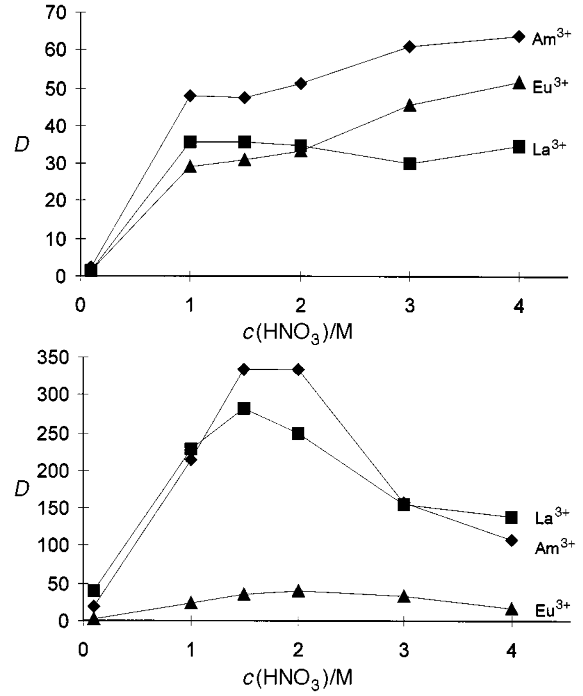


Fig. 4 Distribution coefficients (*D*) of americium, lanthanum and europium as a function of $c(HNO_3)$ for ligands **3c** (above) and **2** (below). Aqueous phase: $c_{Ln} = 10^{-5}$ M, organic phase: $c_L = 10^{-3}$ M in *o*-nitrophenyl hexyl ether.

Compounds **3b** and **3c** have also different selectivity profiles to that seen for **2**. As we have previously described,[9] wide rim CMPOs such as **2** discriminate both between trivalent actinides and lanthanides and among trivalent lanthanides. With **2** and **3a** the light lanthanides (larger cationic radius) are extracted more efficiently than the heavy lanthanides (smaller cationic radius). In contrast a reverse order is seen for compounds **3b** and **3c**. Thus D_{Am}/D_{Eu} for **3c** at 3 M HNO_3 is 1.3 and for **2** is 4.9 whereas D_{Am}/D_{La} is 2.0 for **3c** and 1.0 for **2**. In this way the behaviour of the flexible narrow rim compounds **3b**,**c** is similar to that seen for the simple CMPO ligand **1**. This confirms that for the wide rim compounds **2** and the narrow rim compound **3a** with the shortest spacer pre-organisation onto the rigid calixarene skeleton imparts selectivity of extraction but this is lessened to a degree if the ligand becomes more flexible. However, pre-organisation is still an overriding factor in enhancing extraction of all lanthanides and actinides in comparison to the simple ligand **1**.

Conclusion

The readily available narrow rim CMPOs **3a**–**c** are, like their wide rim congeners (*e.g.* **2**) much more efficient extractants for lanthanides and actinides than CMPO **1** itself. In comparison to **2**, they are considerably better extractants for thorium and their extraction ability does not decrease for nitric acid concentrations higher than 2 M. First experiments also suggest a higher long term resistance towards nitric acid. The strong increase in extraction observed for **3c** in comparison to **3a**,**b** justifies the study of derivatives with even longer spacers which are currently being synthesised. We also are investigating the effect of alteration of the substituent at the wide rim on the extraction properties of narrow rim CMPOs for example increasing the lipophilicity through *p-tert*-octyl groups.

Experimental

Syntheses

^{1}H NMR spectra were recorded at 200 MHz, δ values are given in ppm and J values in Hz. Melting points were determined on Dr Tottoli's (Büchi) melting point apparatus and are uncorrected. FD mass spectra were recorded on a Finnigan MAT 8230 spectrometer. Column chromatography was performed using silica gel (particle size 0.040–0.063 mm) and TLC on silica gel 60 F_{254} plates (Merck). Combustion analysis resulted in most cases in C, N values lower than calculated, a phenomenon often encountered with calixarenes. We do not see any sense, however, in adjusting these values by arbitrarily chosen fractions of included solvent. All compounds were structurally characterised by ^{1}H NMR and mass spectra, their purity was additionally confirmed by TLC.

Calix[4]arene tetraether 4b. A suspension of 10 g (15.4 mmol) *p-tert*-butylcalix[4]arene in DMF (200 ml) was stirred under argon for 30 min. NaH (3.12 g, 130 mmol) and DMF (320 ml) were added and stirring continued for 1 h. *N*-(Bromopropyl)phthalimide (33.1 g, 130 mmol) was then added and the mixture stirred for 5 days at room temperature. After addition of water (100 ml) the resulting precipitate was collected, dissolved in chloroform (200 ml) and washed with 15% HCl (50 ml). Evaporation of the solvent, after drying ($MgSO_4$), followed by precipitation from chloroform–methanol gave the crude product. Chromatography (chloroform–hexane 4:1) yielded the desired compound as a white solid (11.6 g, 54%). Mp 213–215 °C; $\delta_H(CDCl_3)$ 1.03 (36 H, s, *t*-Bu), 2.38 (8 H, quin, J 7.3, $C\mathit{H}_2CH_2N$), 3.10 (4 H, d, J 12.7, $ArC\mathit{H}_2Ar$), 3.86 (8 H, t, J 7.1, $C\mathit{H}_2N$), 3.97 (8 H, t, J 7.3, $OC\mathit{H}_2$), 4.35 (4 H, d, J 12.7, $ArC\mathit{H}_2Ar$), 6.71 (8 H, s, Ar), 7.59 (8 H, m, Ar-Phth), 7.69 (8 H, m, Ar-Phth); FD-MS: *m*/*z* 1398.8 (M^+); $R_f = 0.44$ (chloroform–methanol 30:1) (Found: C, 75.5; H, 7.0; N, 3.9. $C_{88}H_{92}N_4O_{12}$ requires C, 75.6; H, 6.6; N, 4.0%).

Calix[4]arene tetraether 4c. Prepared in an analogous manner to **4b**. Yield 42% after chromatography with chloroform. Mp 138–141 °C; $\delta_H(CDCl_3)$ 1.05 (36 H, s, *t*-Bu), 1.75 (8 H, br m, $C\mathit{H}_2CH_2NH_2$), 2.08 (8 H, br m, $OCH_2C\mathit{H}_2CH_2$), 3.08 (4 H, d, J 12.7, $ArC\mathit{H}_2Ar$), 3.75 (8 H, t, J 7.3, $C\mathit{H}_2N$), 3.90 (8 H, t, J 7.6, $OC\mathit{H}_2$), 4.34 (4 H, d, J 12.2, $ArC\mathit{H}_2Ar$), 6.73 (8 H, s, Ar), 7.61 (8 H, m, Ar-Phth), 7.70 (8 H, m, Ar-Phth); FD-MS: *m*/*z* 1453.8 (M^+); $R_f = 0.45$ (chloroform–methanol 30:1).

Tetraaminocalix[4]arene 5b. Hydrazine hydrate (13.3 ml, 273 mmol) was added to a suspension of 2.00 g (1.43 mmol) of **4b** in ethanol (60 ml). The mixture was heated at reflux for 12 h, cooled and then diluted with water (100 ml). A precipitate formed which was extracted into dichloromethane (4 × 50 ml). The organic layer was then dried ($MgSO_4$) and the solvent evaporated to give the title compound (1.22 g, 98%). Mp 197–201 °C; $\delta_H(CDCl_3)$ 1.05 (36 H, s, *t*-Bu), 2.14 (8 H, quin, J 7.32, $C\mathit{H}_2CH_2N$), 2.27 (8 H, br s, NH_2), 2.91 (8 H, t, J 7.1, $C\mathit{H}_2NH_2$), 3.11 (4 H, d, J 12.2, $ArC\mathit{H}_2Ar$), 3.89 (8 H, t, J 7.1, $OC\mathit{H}_2$), 4.33 (4 H, d, J 12.2, $ArC\mathit{H}_2Ar$), 6.75 (8 H, S, Ar); FD-MS: *m*/*z* 878.8 (M^+).

Tetraaminocalix[4]arene 5c. Prepared in an analogous manner to **5b**. Yield 96%. Mp 195–200 °C; $\delta_H(CDCl_3)$ 1.05 (36 H, s, *t*-Bu), 1.58 (8 H, br m, $C\mathit{H}_2CH_2NH_2$), 1.98 (8 H, br m, $OCH_2C\mathit{H}_2CH_2$), 2.54 (8 H, br s, NH_2), 2.80 (8 H, t, J 7.1, $C\mathit{H}_2NH_2$), 3.10 (4 H, d, J 12.7, $ArC\mathit{H}_2Ar$), 3.85 (8 H, t, J 7.6, $OC\mathit{H}_2$), 4.34 (4 H, d, J 12.7, $ArC\mathit{H}_2Ar$), 6.72 (8 H, s, Ar); FD-MS: *m*/*z* 934.2 (M^+).

Tetraaminocalix[4]arene 5a. NaN_3 (405 mg, 6.21 mmol) was added to a solution of tetrakis[(4-methylphenyl)sulfonyloxyethoxy]-*p-tert*-butylcalix[4]arene[12] (1.50 g, 1.035 mmol) in DMF (20 ml). The solution was then stirred at 60 °C under argon for 4 h, cooled and diluted with water (200 ml). The resulting suspension was extracted with diethyl ether (4 × 75 ml). The combined organic layers were washed with water, dried ($MgSO_4$) and the solvent removed *in vacuo*.

A catalytic amount of Pd/C was added to a solution of the resulting oil in dioxane–ethanol (1:1). H_2 gas was admitted and the mixture stirred for 48 h. The mixture was filtered through a Celite® bed and the solvent evaporated to give the crude amine as a pale green foam. This material was used without further purification. $\delta_H(CDCl_3)$ 1.06 (s, 36 H, *t*-Bu), 2.70 (br, 8 H, NH_2), 3.17 (m, 12 H, $ArC\mathit{H}_2Ar + C\mathit{H}_2NH_2$), 3.93 (t, 8 H, J 5.4, $OC\mathit{H}_2$), 4.33 (d, 4 H, J 12.2, $ArC\mathit{H}_2Ar$), 6.81 (s, 8 H, Ar); FD-MS: *m*/*z* 821.7 (M^+).

General procedure for the preparation of narrow rim CMPO calix[4]arenes

p-Nitrophenyl (diphenylphosphoryl)acetate (2.18 g, 5.7 mmol) and **5a**, **5b** or **5c** (1.14 mmol) were heated at 50 °C in toluene (40 ml) for 18 h. The solvent was then evaporated and the residue taken up in chloroform. The solution was washed repeatedly with 5% Na_2CO_3, dried ($MgSO_4$) and the solvent removed *in vacuo*. Recrystallisation from chloroform–hexane or column chromatography gave the title compounds.

Calix[4]arene 3a. Yield 64% as a buff solid after chromatography with chloroform–hexane 4:1 and precipitation from dichloromethane–hexane. Mp 158–163 °C. $\delta_H(CDCl_3$ + 1 drop DMSO-$d_6)$ 0.90 (36 H, br s, *t*-Bu), 2.82 (4 H, d, J 12.7, $ArC\mathit{H}_2Ar$), 3.30 (8 H, d, J 13.2, $POC\mathit{H}_2CO$), 3.49 (8 H, br m, $NHC\mathit{H}_2$), 3.69 (8 H, br m, $OC\mathit{H}_2$), 3.92 (4 H, d, J 12.7, $ArC\mathit{H}_2Ar$), 6.54 (8 H, br s, Ar), 7.12–7.64 (40 H, m, P-Ar), 8.27 (4 H, br s, NH); R_f 0.32 (chloroform–methanol 9:1). MALDI-TOF MS: *m*/*z* 1791.1 (MH^+), 1813.2 (MNa^+), 1829.0 (MK^+), 1898.0 (MAg^+).

Calix[4]arene 3b. Yield 75%. Mp 244–246 °C. δ_H (200 MHz, $CDCl_3$) 1.04 (36 H, s, *t*-Bu), 1.99 (8 H, br m, $C\mathit{H}_2CH_2N$), 3.00 (4 H, d, J 12.2, $ArC\mathit{H}_2Ar$), 3.27 (8 H, br m, $C\mathit{H}_2N$), 3.48 (8 H, d, J 14.1, $POC\mathit{H}_2CO$), 3.65 (8 H, br t, $OC\mathit{H}_2$), 4.14 (4 H, d, J 12.7, $ArC\mathit{H}_2Ar$), 6.71 (8 H, s, Ar), 7.31–7.78 (40 H, m, P-Ar), 8.27 (4 H, br m, NH); FD-MS: *m*/*z* 1848.4 (M^+); R_f 0.40 (chloroform–methanol 9:1).

Calix[4]arene 3c. Yield 78%. Mp 232–236 °C; $\delta_H(CDCl_3)$ 1.05 (36 H, s, *t*-Bu), 1.41 (8 H, br m, $C\mathit{H}_2CH_2NH_2$), 1.82 (8 H, br m,

$OCH_2CH_2CH_2$), 3.07 (4 H, d, *J* 12.7, $ArCH_2Ar$), 3.15 (8 H, br, CH_2NH), 3.56 (8 H, d, *J* 14.2, $POCH_2CO$), 3.85 (8 H, br t, OCH_2), 4.23 (4 H, d, *J* 12.2, $ArCH_2Ar$), 6.73 (8 H, s, Ar), 7.38–7.84 (40 H, m, P-Ar), 8.28 (4 H, br s, NH); FD-MS: *m*/*z* 1902.0 (M^+); R_f 0.29 (chloroform–methanol 9 : 1).

Extraction

Materials. Thorium(IV) and lanthanides(III) were used as the nitrates: $Th(NO_3)_4 \cdot 5H_2O$ (Merck, pa), $La(NO_3)_3 \cdot H_2O$ (Fluka, puriss), $Pr(NO_3)_3$ (Strem Chemicals), $Tb(NO_3)_3$ (Merck), and $Er(NO_3)_3$ were used as purchased, while $Eu(NO_3)_3 \cdot xH_2O$ and $Yb(NO_3)_3 \cdot xH_2O$ were prepared by reaction of the corresponding carbonates with a nitric acid solution (Carlo Erba, 65% pa) following the literature procedure.[13] Stock solutions were standardised by complexometric titrations with EDTA in the presence of the appropriate indicator. Arsenazo(III) (Aldrich) was used for the spectrophotometric determination of Ln(III) and Th(IV) during extraction experiments.[6]

Extraction of lanthanides(III) and thorium(IV) with dichloromethane. The aqueous phase consisted of solutions of lanthanide or thorium nitrates (10^{-4} M) in 1 M HNO_3 and the organic phase of solutions of the calixarenes in dichloromethane, at appropriate concentrations to give extraction percentages ranging from 10 to 90%. 1 ml of each phase was put in a stoppered tube and stirred at 20 °C during 12 h. After separation of the two phases, the concentration of the cation remaining in the aqueous phase was monitored spectrophotometrically using Arsenazo(III) (2,2′-[1,8-dihydroxy-3,6-disulfonaphthalene-2,7-diylbis(azo)]bis(benzenearsonic acid)) as coloured reagent. The Arsenazo solution was prepared by dissolving the reagent in a sodium formate–formic acid buffer (pH = 2.8). 5 ml of this solution (6.4×10^{-4} M) were then added to a 0.65 ml aliquot of the aqueous phase and the volume adjusted to 50 ml with the buffer. The absorbances *A* were determined at 665 nm for Th(IV) and 655 nm for Ln(III). Since the concentration of Arsenazo is 30 times higher than the concentration of the cations, complete complexation can be assumed. The percentage of cation extracted was calculated as $\%E = 100[A_1 - A/(A_1 - A_0)]$, where A_0 is the absorbance of the Arsenazo solution without the cation and A_1 the absorbance of the Arsenazo solution containing the known concentration of cation before extraction.

Extraction of lanthanides and americium(III) with *o*-nitrophenyl hexyl ether. An aqueous phase was prepared at varying concentrations of nitric acid (0.01–4 M). Inactive lanthanides (La, Ce, Nd, Sm and Eu) were included at concentrations of 10^{-5} M. Americium, as the radioisotope ^{241}Am, was added at a concentration of 10^{-9} M to give an activity of approximately 1000–1500 kbq dm^{-3}. A 3 ml aliquot was then shaken at room temperature for one hour with a 3 ml aliquot of the organic phase ($c_L = 10^{-3}$ M in *o*-nitrophenyl hexyl ether (NPHE)). After centrifugation the concentration of the lanthanides and actinides in the aqueous phase was determined by ICP-MS (Inductively Coupled Plasma Mass Spectrometry) using an ICP-MS, ELAN-5000 (Perkin Elmer). The distribution coefficient $D = \Sigma[M]_{org}/\Sigma[M]_{aq}$ was calculated from the metal concentrations in the aqueous phase determined before (c_0) and after extraction (c) as $D = (c_0 - c)/c$.

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