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tert-Butyl-calix[4]arenes Substituted at the Narrow Rim with Cobalt Bis(dicarbollide)(1–) and CMPO Groups – New and Efficient Extractants for Lanthanides and Actinides

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Calix[4]arene derivatives bearing two residues $\mathbf{A}^{(-)}$ derived from cobalt bis(dicarbollide)(1–) (**1**) and two CMPO groups **B** at their narrow rim were synthesized from *t*Bu-calix[4]arene in four steps. The first step involved the preparation of *t*Bu-calix[4]arene diether derivatives with appropriate precursors for amino groups (mostly nitriles **3**). These were *O*-alkylated through ring-opening reactions with the zwitterionic dioxane derivative $[(8\text{-}O(CH_2CH_2)_2O\text{-}1,2\text{-}C_2B_9H_{10})\text{-}(1',2'\text{-}C_2B_9H_{11})\text{-}3,3'\text{-}Co]^0$ (**10**) to produce ionic nitrile derivatives **4**. Reduction of the nitrile groups with $BH_3{\cdot}SMe_2$ (or deprotection in the case of the corresponding phthalimido or Boc derivatives **8**) led to a series of diamines **5a–f**, which were subsequently converted into the corresponding CMPO derivatives **6a–f** by acylation with *p*-nitrophenyl(diphenylphosphoryl) acetate. Pure *cone* conformers were isolated in moderate to excellent yields after the second or third reaction step, although the presence of other conformers in the reaction mixtures was sometimes observed by NMR spectroscopy and HPLC, and in one case a di-$\mathbf{A}^{(-)}$-di-**B** derivative **6c*** in the *1,3-alternate* conformation was prepared. The novel ionic ligands **6a–f** showed dramatically enhanced extraction abilities for trivalent actinides and lanthanides in relation to the previously reported simple covalent combination of one $\mathbf{A}^{(-)}$ with one **B** group or to various synergistic mixtures of calixarenes substituted exclusively with two $\mathbf{A}^{(-)}$ or two **B** moieties. A 1:1 mixture of calix[4]arenes containing four $\mathbf{A}^{(-)}$ anions (**13**) and four CMPO functions (**14**), however, showed similarly high extraction efficiency, comparable to that of the best calixarenes **6b–d** with mixed substitution. Complexation studies with **6c** for La^{3+}, Eu^{3+} and Yb^{3+} in methanol carried out by UV spectrophotometry and microcalorimetry revealed the formation of 1:1 and 1:2 metal-to-ligand complexes with $\log\beta$ values ranging from 9.6 to 11.7.

Introduction

There is still strongly growing interest in using calix[4]arenes[1–3] as basic platforms for the assembly of various functional groups in predefined spatial arrangements. Indeed, designed attachment of metal binding groups on calixarene platforms has provided efficient calixarene-based extraction systems suitable for partitioning of the radionuclides ^{137}Cs[4,5] and ^{90}Sr,[6,7] as well as lanthanides and actinides,[8] from strongly acidic high-level activity nuclear waste (HLW). Their efficiency and selectivity are achieved by incorporation of several (potentially different) chelating groups at the narrow and/or wide rims of the calixarene platform, where the preorganized arrangement allows for their cooperative action. Among the most efficient compounds of this series are calix[4]arenes functionalized with carbamoyl methyl diphenyl phosphane oxide (CMPO) **B** (Figure 1) groups at the wide[8] or narrow rim.[8–10] However, the use of calixarenes and other organic ionophores in the partitioning of radionuclide cations from strongly acidic HLW is often accompanied by the unwanted co-transport of nitrate ions into the organic phase. A positive synergistic

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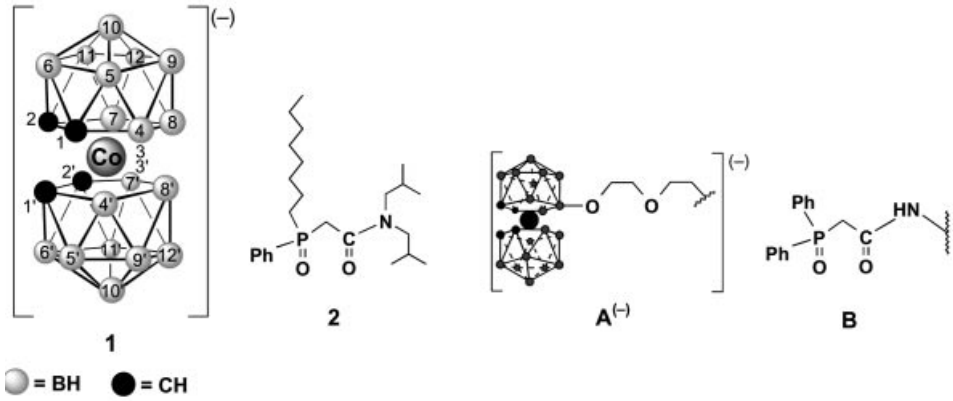


Figure 1. Schematic presentations of cobalt bis(dicarbollide) ion (**1**), the technically used CMPO (**2**) and of the structural elements $\mathbf{A}^{(-)}$ and **B** derived from them.

effect of the cobalt bis(dicarbollide)(1–) anion **1** has been observed for the extraction of M^{3+} with various organic ligands capable of tightly complexing lanthanides and actinides.[11] This has also been reflected in theoretical and molecular modelling studies.[12]

The singly charged cobalt bis(dicarbollide)(1–) ion **1** (Figure 1)[13] – $[(1,2\text{-}C_2B_9H_{11})_2\text{-}3\text{-}Co]^-$, named Cosan in the following text – belongs to the class of electron-deficient 26-electron 12-vertex icosahedral *closo* borane clusters of extraordinarily high chemical and thermal stability, hydrophobicity and inorganic superacid behaviour.[13,14] Halogen derivatives of **1** were designed more than 25 years ago for the efficient extraction of $^{137}Cs^+$ and $^{90}Sr^{2+}$ from highly acidic nuclear waste.[11] This liquid–liquid extraction procedure has been developed into an industrial process currently called "UNEX".[15,16] New compounds of this class incorporating phosphorus-containing ligands that show efficiency for the extraction of trivalent α-emitters have recently been developed.[17–19]

Cobalt bis(dicarbollide) anions are able to compensate the positive charge of the radionuclide intermolecularly and thus to reduce or eliminate the nitrate co-transport when used in synergistic mixtures with various organic ionophores. Covalent bonding of hydrophobic cluster anions to the calixarene platform is expected to provide more intimate intramolecular charge compensation and can lead to increased hydrophobicity and solubility of the extracting complex particle. This can improve the efficiency and stability of the whole extraction system.

We have recently reported various methods by which to attach ionic boron clusters $\mathbf{A}^{(-)}$ covalently to calix[4]arene and resorc[4]arene platforms.[20] However, no further ligating groups were present in these molecules, and such species were therefore not efficient enough for the extraction of trivalent radionuclides and only mimicked the extraction behaviour of the parent ion **1** or its halogenated analogues. Without addition of synergists, these species were able to extract only Cs^+.

In this paper we present a detailed report on the synthesis of calix[4]arenes simultaneously substituted at their narrow rims in alternating order with two hydrophobic cluster anions $\mathbf{A}^{(-)}$ and two CMPO functions **B** (for a schematic presentation of their structures see Figure 1). Results from extraction[21] and complexation studies based on these compounds are also presented.

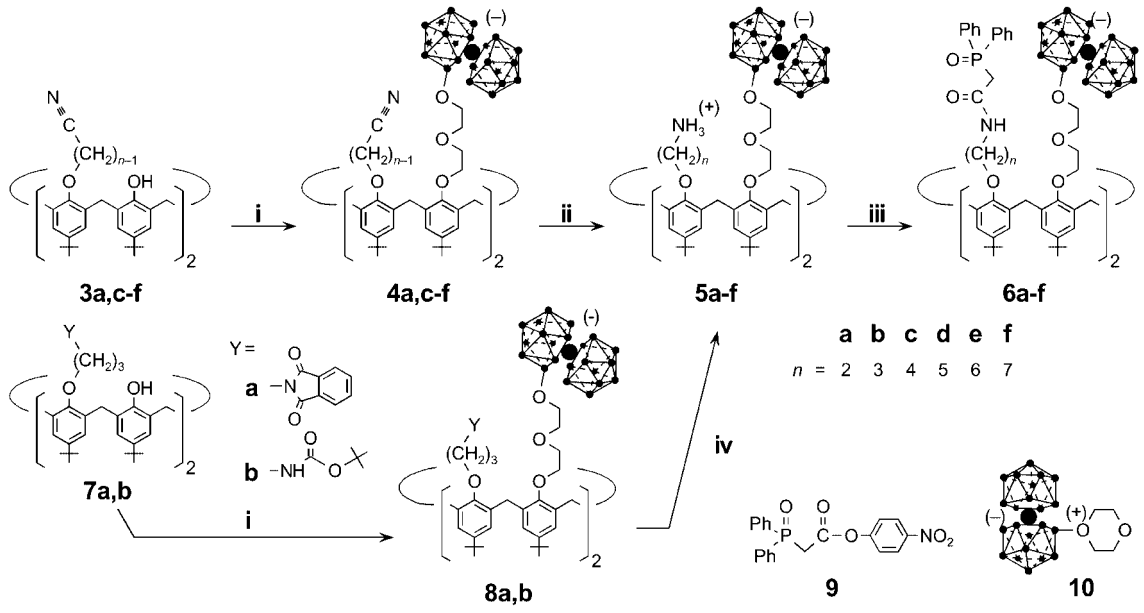
Results and Discussion

Synthesis

One to four Cosan groups $\mathbf{A}^{(-)}$ can be bound to the narrow rim of *t*Bu-calix[4]arene through a diethylene glycol spacer by using the dioxane derivative **10** as an *O*-alkylating reagent.[20] CMPO functions are usually attached to the narrow rim in three steps (*O*-alkylation with *N*-(ω-bromoalkyl)phthalimide or ω-bromonitrile, deprotection of the amino group or reduction of the nitrile, and acylation of the amino groups with the active ester **9**).[9,10]

Among several possibilities we chose to introduce the precursor to the amino function in the first step,[22] mostly by alkylation with an ω-bromonitrile. The following steps are illustrated in Scheme 1.

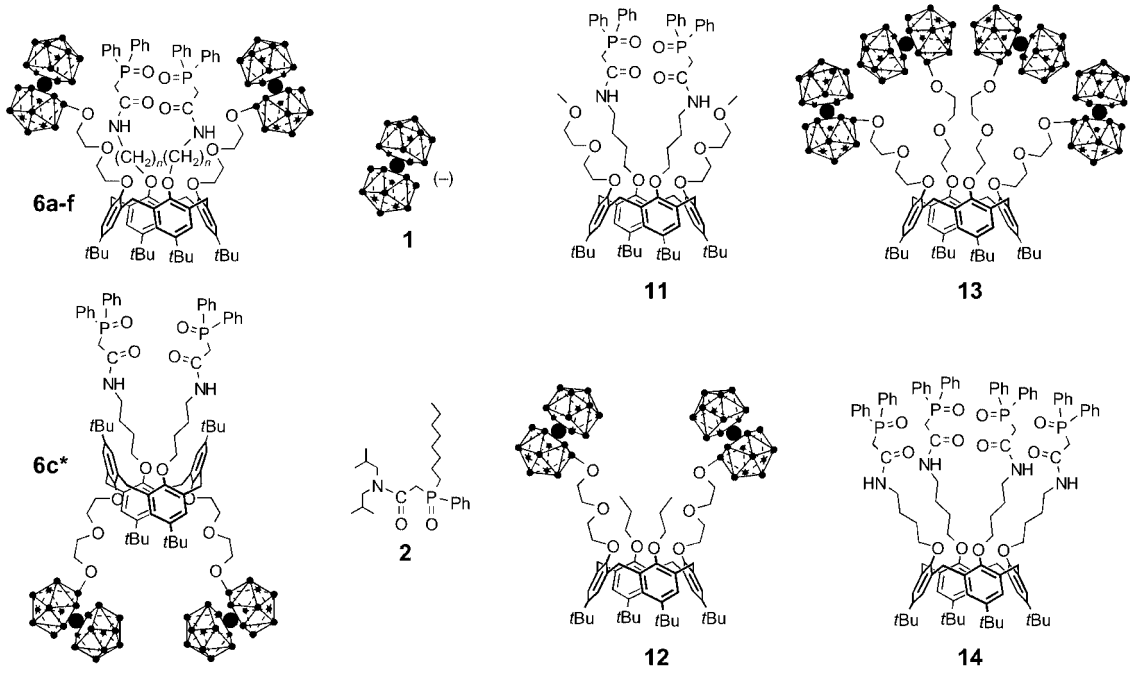
1,3-Dinitriles **3**, easily available as *syn* isomers for $n = 2$ and 4–7 (for $n = 3$, see below), were treated with two equivalents of **10**[20–23] in toluene/DME at room temperature in the presence of NaH as base for the deprotonation. In the case of **3a** the formation of the almost pure *cone* isomer was indicated by the NMR spectrum of the crude product, and **4a** was isolated in 76% yield. High yields of pure compounds **4d**–**f**, ranging from 66 to 74%, were also isolated, while in the case of **4c** the reaction mixture was more complicated. NMR spectra indicated the presence of the *1,3-alternate* isomer **4c*** in comparable quantities and the mixture could be separated by fractional crystallization of the Cs^+ salts from aqueous ethanol, in which the *cone* isomers accumulated in the mother liquors, or more conveniently (as applied for **4d**–**f**) from benzene/hexane, from which the *cone* isomers crystallized out preferentially. Pure *cone* isomer **4c** was finally obtained in moderate yields of 25–30% by flash chromatography (CH_2Cl_2/acetonitrile). The reason for the increased tendency for $n = 4$ to form the *1,3-alternate* isomer is not entirely clear. It was not observed for



Scheme 1. Synthesis of *t*Bu-calix[4]arenes substituted at their narrow rims with two anionic groups $\mathbf{A}^{(-)}$ and two CMPO fragments **B**. i) NaH, **10**, toluene/DME, room temp.; ii) $BH_3{\cdot}S(CH_3)_2$ (excess), THF, room temp.; iii) NaH, **9**, THF, 60 °C; iv) for **8a**: aq. $H_4N_2{\cdot}H_2O$, EtOH, reflux, or for **8b**: CF_3COOH, CH_2Cl_2, 0 °C.

the tetra-*O*-alkylation of *t*Bu-calix[4]arene by **10**, but was already observable with the 1,3-dipropyl ether of *t*Bu-calix[4]arene.[20] Most probably a low solubility of the sodium salt of **3c** in the reaction mixture played some role. However, these facts stimulated the synthesis of **4c***, which was (nearly) the only product formed when Cs_2CO_3 was employed as a base (isolated in 48% yield by crystallization from hot aqueous ethanol followed by chromatography).

The second reaction step in Scheme 1, the reduction of the conformationally pure dinitrile derivatives **4** to the corresponding diamino derivatives **5**, was accomplished with $BH_3{\cdot}SMe_2$ in THF. Alternatively, the reduction of the nitriles can be performed directly with the toluene/DME solution obtained in the first reaction step. These reactions proceeded smoothly with good yields. The zwitterionic amino derivatives **5** were isolated after acid hydrolysis, chromatog-



Scheme 2. Compounds used in extraction studies.

raphy and recrystallization from methanol. In the case of **5c/5c***, almost pure **5c*** crystallized during the first recrystallization from benzene/hexane when the reduction was carried out with a mixture of the two conformers, offering another possibility for the separation of the *cone* and the *1,3-alternate* isomers at this stage.

Compound **3b** could not be prepared by *O*-alkylation with bromopropionitrile because the formation of acrylonitrile through HBr elimination predominates. In this case the amino derivative **5b** was prepared by the two alternative ways shown in the bottom part of Scheme 1. Either the diphthalimide (**7a**) or the BOC-protected diaminopropyl ether (**7b**) were further *O*-alkylated with **10** under standard conditions to give 52% and 61% yields of the *cone* isomers of **8a** or **8b**. Deprotection of the amino groups, either by hydrazinolysis (for **8a**) or by acid hydrolysis with CF_3COOH (for **8b**), gave the amino derivative **5b** in overall yields of about 75% in both cases. This demonstrates that both protective groups can be used in the presence of the cobalt bis(dicarbollide) system.

All the diamines **5**, including the *1,3-alternate* isomer **5c***, were easily converted into the corresponding CMPO derivatives **6** and **6c*** by *N*-acylation with the active ester **9**. The reactions proceeded smoothly at 60 °C in THF and the expected products were obtained in high yields. In this manner, a complete series with spacers of two to seven methylene groups between the CMPO function and the calixarene platform were obtained.

The model compound **11** (see Scheme 2) used for comparative extraction studies was prepared analogously. 1,3-Di-*O*-alkylation of *t*Bu-calix[4]arene with methoxy-ethoxy-ethyl chloride, followed by exhaustive alkylation with γ-bromobutyronitrile, produced a tetraether in the *cone* conformation, which was converted into **11** by reduction and acylation as described for the conversion of **4** into **6**. Compounds **12** and **13** were prepared by *O*-alkylation of the 1,3-dipropyl ether and the parent *t*Bu-calix[4]arenes with **10**.[20]

Structural Studies

The ^{11}B NMR spectra of all the compounds **4**–**6** closely resemble those of the previously reported 8-*O*-alkoxy-substituted Cosans,[17,19] including calix[4]arene derivatives.[20] The ^{11}B NMR assignments were made through analogy with anion **1** substituted with simpler groups, though peak broadening and overlaps were observed in the spectra of most of the species containing two $\mathbf{A}^{(-)}$ residues for skeletal positions B(4,7), B(9,9′;12,12′), B(5,11) and B(6′), especially in the case of amino derivatives. The ^1H NMR spectra of **4a**, **4c**–**f**, **5a**–**f**, **6a**–**f**, **8a** and **8b** are completely in agreement with the C_{2v} symmetry of a tetrasubstituted calix[4]arene bearing two different substituents in alternating fashion. Two singlets for aromatic protons, two doublets with geminal coupling for the methylene bridges and two singlets for the *tert*-butyl groups are found, in the expected intensities. The ratios of the cage CH signals vs. the corresponding calix[4]arene signals in the ^1H NMR spectra are in accordance with the presence of two $\mathbf{A}^{(-)}$ residues. The main difference between the *cone* **4c** and the *1,3-alternate* **4c*** conformers consists of the collapse of the two doublets of the methylene bridges from an AX system ($\Delta\delta$ = 1.15 ppm) into an AB system ($\Delta\delta$ = 0.095 ppm).[3,28] In the spectra of the amino derivatives **5a**–**f**, signal broadening for the ArH and equatorial protons of the methylene bridges was often observed. The ^1H NMR spectra of all CMPO derivatives **6a**–**f** exhibit well distinguished aromatic signals for the phenyl end groups with relative intensities of 2:1:2 along with the ^{31}P doublet of the CH_2-P resonance. The $^{31}P\{^1H\}$ spectra each show a singlet near 30 ppm.

Electrospray mass spectrometry was used for the further characterization of all compounds **4**–**6** and **8**. In most cases negative ions corresponding to the molecular ion were observed, with 100% abundance for the highest peak in the isotopic distribution plot. The zwitterionic derivatives **5a**–**f** displayed the $[M - H]^-$ peak, while dianions (e.g., **4a**, **4c**–**f**, **6a**–**f**) showed $[M]^{2-}$ peaks in all cases. The isotopic distributions in the boron plots of these peaks are in agreement with the charge, showing distances of 1/2 mass units for dianionic compounds.

Extraction Studies

The novel calix[4]arene derivatives **6** were checked for the extraction of europium and americium from acidic solution and compared with selected model compounds. A formula survey is given in Scheme 2.

Preliminary results carried out for an extractant concentration of $c = 1 \times 10^{-3}$ M indicate exceptionally high Eu/Am distribution coefficients even from strongly acidic solutions. For a reasonable comparison of extractabilities of different compounds within the series, the concentrations had to be reduced to 1×10^{-5} M, due to high extraction power at higher concentrations. Table 1 contains the extraction results for compounds **6a**–**f** with europium and americium. It can be seen that Eu/Am are extracted well from 0.1 and 0.4 M HNO_3 by practically all tested compounds and by **6b**–**e** even from 1 M acid. Distribution coefficients greater than 100 for $c(HNO_3)$ = 0.4 M and nearly 10 for $c(HNO_3)$ = 1.0 M are unprecedented for such low concentrations of extractants. Further increases in acidity lead to marked decreases in the extraction efficiencies and the distribution ratios in 4 M acid are low.

The Eu/Am extraction by **6a**, with the shortest CMPO arms, is considerably lower, probably due to the different distances of the Cosan and the CMPO groups from the calixarene platform. Steric crowding and the low flexibility of the short connecting link (n = 2) could be further reasons. With **6f**, with the longest CMPO arms, a considerable drop in the extraction efficiency is again observed. In this case, it is probably the high flexibility of both linkers and the long distance between CMPO and Cosan functions and the calixarene platform that introduce geometric imperfections for their cooperative action. Since the extraction abilities of **6b**, **6c** and **6d** – the compounds with three, four

Table 1. Eu and Am extraction data for compounds **6a**–**f** bearing two anionic groups $\mathbf{A}^{(-)}$ and two complexing groups **B**.[a]

Compound	D	$c(HNO_3)$				
		0.1	0.4	1.0	2.0	4.0
6a	D_{Eu}		3.87	0.208	0.0241	<0.01
$n = 2$	D_{Am}		4.28	0.227	0.0236	<0.01
6b	D_{Eu}	>100	>100	7.73	0.784	0.0538
$n = 3$	D_{Am}	>100	>100	9.37	0.837	0.0435
6c	D_{Eu}	>100	>100	7.00	0.647	0.0352
$n = 4$	D_{Am}	>100	>100	7.52	0.681	0.0290
6d	D_{Eu}	>100	>100	6.09	0.443	0.0203
$n = 5$	D_{Am}	>100	>100	8.21	0.562	0.0206
6e	D_{Eu}	>100	43.5	4.41	0.729	0.105
$n = 6$	D_{Am}	>100	76.7	2.78	0.742	0.0670
6f	D_{Eu}		4.54	0.422	0.0850	0.0101
$n = 7$	D_{Am}		6.01	0.496	0.102	0.0260

[a] 1.2×10^{-5} M extractant in HMK/TPH mixture 1:1; HMK = octan-2-one, TPH = hydrogenated tetrapropylene.

and five carbon spacers – are approximately equal, compound **6c** was selected as representative for more detailed studies. Table 1 also shows that Am and Eu are extracted by all compounds to approximately the same extent. This makes an effective separation impossible, but it allows to focus in the following on Eu alone.

To compare the extraction ability of **6c**, which is fixed in the *cone* conformation, with that of its *1,3-alternate* isomer **6c***, the concentration must be raised to 10^{-3} M (see Table 2). With nitrobenzene as diluent, the distribution coefficients for **6c** and Eu are now >100 for all concentrations of HNO_3. For **6c*** they are about 100 for $c(HNO_3) = 0.01$–0.1, but D drops to 11, 1.6 and 0.21 for $c(HNO_3) = 1.0$, 2.0 and 4.0 M. This means that **6c** is about two orders of magnitude more effective than **6c***. Obviously, the mutual orientation of the "complexing groups" **B** and the charge-compensating groups $\mathbf{A}^{(-)}$ has a drastic influence on the extraction ability.

Table 2. Extraction of Eu (and Am) by compounds **6c** (fixed in the *cone* conformation) and **6c*** (fixed in the *1,3-alternate* conformation).[a]

Compound	D	$c(HNO_3)$			
		0.01	0.1	1.0	2.0
6c (*cone*)	D_{Eu}	>100	>100	>100	>100
6c* (*1,3-alternate*)	D_{Eu}	94.2	>100	10.6	1.55
	D_{Am}	>100	>100	23.9	3.34

[a] 1×10^{-3} M extractant in nitrobenzene.

The extraction ability of **6c** is high in all the studied diluents with the exception of *n*-octanol (see Table 3). For a concentration of 10^{-3} M the distribution coefficient for Eu is >100 up to $c(HNO_3) = 1.0$ M. A further increase in the HNO_3 concentration leads to decreasing D values in the order HMK < DCE < NB < HMK/TPH (HMK = octan-2-one, DCE = 1,2-dichloroethane, NB = nitrobenzene, TPH = hydrogenated tetrapropylene). For the last diluent, a reasonable extraction is found even for $c(HNO_3) = 6$ M. Obviously the difference in the dielectric constants of the solvents has no significant effect. Replacing nitrobenzene (ε = 38) by the HMK/TPH mixture ($\varepsilon \approx 5$) does not lead to any remarkable difference in the extraction efficiency of **6c**. Therefore, HMK/TPH, in which the concentration can be raised to approx. 0.1 M, is a reasonable alternative to polar solvents.

The decreasing distribution coefficients under strongly acid conditions indicate the possibility of Eu stripping, provided that the extractant is sufficiently stable in such a medium. In fact, the chemical stability of **6c** is good. With a 10^{-3} M solution in HMK/TPH 1:1, no decrease in the distribution coefficients was observed after 32 d, with shaking of the sample for 2 h per day with 3 M HNO_3. Preliminary radiation tests established an excellent stability of **6c** up to a 100 kGy dose, while the distribution coefficient decreased from 4.3 to 1.12 at 500 kGy.

The effect of the covalent attachment of two $\mathbf{A}^{(-)}$ groups ***and*** two **B** groups to the narrow rim of a calix[4]arene fixed in the *cone* conformation becomes especially evident on comparison with the model compounds **11** and **12**. Under conditions [$c(HNO_3) = 0.2$ M, c(extractant) = 10^{-5} in HMK/TPH 1:1] where D(Eu) for **6c** is still higher than 100, it is lower than 0.01 for **11**, either alone or in combination with double the amount of **1** (or its hexachloro derivative), for **12**, either alone or in combination with double the amount of **2**, or for an equimolar mixture of **11** and **12**. A synergistic effect of **11** and **12** is seen, however, at $c = 10^{-3}$ M, where D(Eu) for their mixture is similar to that for **6c***.[21]

Surprisingly, however, a synergistic effect was observed for the mixture of tetra-Cosan[20] calix[4]arene **13** and tetra-CMPO calix[4]arene **14** (which is a relatively strong extractant itself).[10] As shown in Table 4, the Eu extraction capabilities of both calixarenes alone are negligible at the low concentration of $c = 5 \times 10^{-6}$ M. However, a 1:1 mixture of **13** and **14** ($c = 5 \times 10^{-6}$ M for each component) shows an extraction efficiency for Eu comparable to that of **6c** ($c = 1 \times 10^{-5}$ M). In the low acidity range, **6c** is a better extract-

Table 3. Extraction of Eu by **6c** in different solvents.[a]

Solvent	$c(HNO_3)$								
	0.001	0.01	0.1	1.0	2.0	4.0	6.0	8.0	10.0
NB	>100	>100	>100	>100	>100	>100	0.659	0.0492	0.0174
HMK/TPH	>100	>100	>100	>100	>100	>100	2.98	0.868	0.331
HMK	>100	>100	>100	>100	15.8	1.97			
n-octanol	>100	17.2	5.87	0.940	0.0168				
1,2-DCE	>100	>100	>100	>100	36.3	2.22	0.210	0.0386	0.0028

[a] $c = 1 \times 10^{-3}$ M **6c** in corresponding solvent; NB = nitrobenzene.

Table 4. Comparison of the extraction efficiency of **6c** with those of model compounds **13** and **14** and their synergistic mixtures in 1,2-dichloroethane.

Compound	Concentration [M]	D_{Eu}		
	$c(HNO_3)$	0.1	1.0	3.0
13	c(**13**) = 5×10^{-6}	$<10^{-3}$	$<10^{-3}$	$<10^{-3}$
14	c(**14**) = 5×10^{-6}	0.0152	0.0226	0.0398
13 + 14	c(**13**) = c(**14**) = 5×10^{-6}	114	1.15	0.125
6c	c(**6c**) = 1×10^{-5}	$> 10^3$	1.50	0.0411
14 + 1	c(**14**) = 5×10^{-6}; c(**1**) = 2×10^{-5}	0.0811	0.0117	0.0126

ant, but D(Eu) is reduced for both systems in the high acidity range, as expected for **14**, and the order of the extraction efficiency is reversed. This is apparently due to the increase in D(Eu) for **14** with increasing acid concentration.[10]

Table 4 also presents data for a mixture of **14** with the parent anion **1** in a molar ratio of 1:4 (corresponding to a concentration of $\mathbf{A}^{(-)}$ and **B** groups identical to that in the **13** + **14** mixture). They clearly show that the presence of four free anions **1** has a much lower effect on the extraction efficiency.

This observation suggests an extraction mechanism in which Eu is trapped either between two molecules of **6c** or by a combination of one molecule **13** with one molecule **14**. Both assemblies offer four CMPO and four Cosan residues preorganized on the narrow rim of a calix[4]arene. This seems to be essential for the formation of a tight complex, which accounts for similarities in the extraction efficiencies of **6c** and of **13** + **14** and explains the very high D(Eu) values observed. Further support is provided by a series of isomolar extractions carried out with compounds **13** and **14** (Figure 2). There is a pronounced optimum for a molar ratio of 1:1, which corresponds to the composition of the calixarene **6c**.

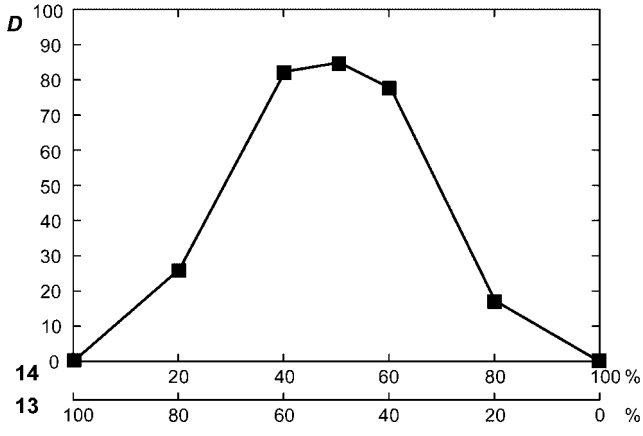


Figure 2. Isomolar series, extraction of Eu from 1 M HNO_3 by mixtures of **13** and **14**, Σ c(**13**) + c(**14**) = 1×10^{-4} M, DCE. The solid line has no physical meaning and is drawn only to guide the reader's eyes.

Complexation studies in a homogeneous system (see below) also indicate the formation of strong 1:2 complexes between M^{3+} cations and the calixarene **6c**.

Complexation in Methanol

The complexing behaviour of ligand **6c** and its model compound without the two cobalt bis(dicarbollide) ions (**11**) towards the three lanthanide cations La^{3+}, Eu^{3+} and Yb^{3+} was studied in methanol by two different techniques: UV absorption spectrophotometry and microcalorimetry. The latter allows the separation of the global stability constant (β) into its enthalpic and entropic contributions. With both ligands, the spectral changes induced by the complexation were small but sufficient to be interpreted using the program Specfit.[23] The factor analysis included in this program indicated in each case the presence of a minimum of two absorbing species: the ligand and one complex. The best model to fit the experimental data involved the formation of a single 1:2 (M:L) species with the three cations studied. Their stability constants (Table 5) do not show any significant selectivity in the series: the logarithms range from 9.6 to 11.2 for **6c** and from 7.2 to 7.5 for **11**.

Table 5. Logarithms of the stability constants of some lanthanide complexes with ligands **6c** and **11** (T = 25 °C, I = 0.01 M Et_4NNO_3).

Ligand	Complex	La^{3+}	Eu^{3+}	Yb^{3+}
6c	1:2	11.1 ± 0.2	11.2 ± 0.6	9.6 ± 0.5
11	1:2	7.54 ± 0.06	7.2 ± 0.1	7.3 ± 0.2

Microcalorimetric titrations performed with **6c** in the same solvent confirmed the formation of 1:2 species as shown by the thermogram represented in Figure 3, which exhibits a breakpoint near c_M/c_L = 0.5. However, instead of becoming flat as would be expected for the formation of a single complex, the curve showed a more or less pronounced decrease for the different cations. This variation could be interpreted in terms of the formation of a second species of 1:1 stoichiometry, the stability of which depends on the cation.

In the case of **11** the thermograms were quite different, with breakpoints close to c_M/c_L = 1 (Figure 3). However, their best interpretation also involved the formation of both 1:1 and 1:2 complexes. The fact that 1:1 species could not be detected by spectrophotometry can be explained by the small spectral changes observed with both ligands during complexation. The formation of ML_2 complexes is quite unusual for narrow rim derivatives of calix[4]arenes. The related narrow rim tetra-CMPO derivatives **14** form only 1:1 complexes with lanthanides in methanol.[24]

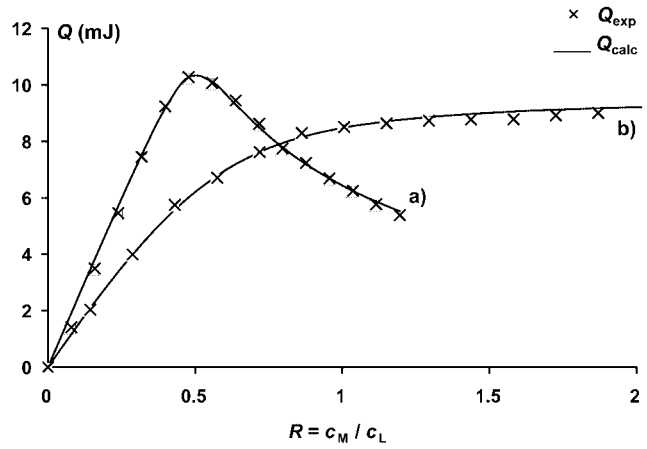


Figure 3. Plots of the heat vs. the metal-to-ligand concentration ratio during the calorimetric titration of **6c** (a) and **11** (b) with europium nitrate in methanol.

Table 6 gives the thermodynamic parameters of these complexes with the two ligands and the three cations studied. The stability constants obtained by microcalorimetry for the ML_2 complexes are of roughly the same order of magnitude as those derived from spectrophotometry; a small difference ($\Delta\log\beta_{12} \approx 0.4$–$2.1$) can be accounted for by the absence of ML complexes in the refinement of the spectrophotometric data. ML_2 complexes with both ligands are almost as stable as the corresponding 1:1 complexes. A slight positive cooperative effect ($\Delta = \log\beta_{12} - 2\times\log\beta_{11} = 0.4$) is even noted with Eu^{3+} and **6c**.

Table 6. Thermodynamic parameters[a] for the complexation of some lanthanide cations with **6c** and **11**, determined by microcalorimetric titration in methanol at 25 °C.

Ligand	Parameter	La^{3+}	Eu^{3+}	Yb^{3+}
6c	$\log\beta_{11}$	5.6	4.9	6.1
	$-\Delta G_{11}$ (kJ mol^{-1})	32	28	35
	$-\Delta H_{11}$ (kJ mol^{-1})	0.6	8.7	1.6
	$T\Delta S_{11}$ (kJ mol^{-1})	31	19	33
	$\log\beta_{12}$	10.7	10.2	11.7
	$-\Delta G_{12}$ (kJ mol^{-1})	61	58	67
	$-\Delta H_{12}$ (kJ mol^{-1})	27	35	39
	$T\Delta S_{12}$ (kJ mol^{-1})	34	23	28
11	$\log\beta_{11}$	5.1	3.9	4.6
	$-\Delta G_{11}$ (kJ mol^{-1})	29	22	26
	$-\Delta H_{11}$ (kJ mol^{-1})	23	19	10
	$T\Delta S_{11}$ (kJ mol^{-1})	6	4	17
	$\log\beta_{12}$	9.3	7.9	9.0
	$-\Delta G_{12}$ (kJ mol^{-1})	53	45	51
	$-\Delta H_{12}$ (kJ mol^{-1})	29	55	16
	$T\Delta S_{12}$ (kJ mol^{-1})	24	10	35

[a] Mean values of at least two independent experiments – $\pm\sigma_{n-1}$: $-\Delta G$(0.6 – 5); $-\Delta H$ (0.05 – 8); and $T\Delta S$ (2 – 12).

There is no pronounced selectivity for **6c** within the series; the stabilities of the 1:1 and 1:2 complexes are similar for La^{3+} and Eu^{3+} and increase slightly for Yb^{3+}. Complexes with **11** are less stable than those with **6c**. These differences in stability increase in the series from La^{3+} to Yb^{3+} ($\Delta\log\beta_{11} = 0.5$–$1.5$ and $\Delta\log\beta_{12} = 1.4$–$2.7$). In other words, the contribution of the cobalt bis(dicarbollide) moieties $\mathbf{A}^{(-)}$ is more important for the smaller Yb^{3+} than for the larger La^{3+}.

The formation of the 1:1 complexes with **6c** is strongly entropy-driven ($T\Delta S_{11}$ is higher than 30 kJ mol^{-1} for La^{3+} and Yb^{3+}), whereas the enthalpy changes in the case of lanthanum are only weakly negative and even close to zero. In contrast, the formation of the ML_2 complex is characterized by a large and favourable enthalpy change ($-\Delta H_2 = -\Delta H_{12} - (-\Delta H_{11}) = 26$–$37$ kJ mol^{-1}) and very small entropy changes. A quite different situation is observed for **11**, where the stabilization of the 1:1 complexes is mostly enthalpic, but with a decrease in $-\Delta H_1$ from La^{3+} to Yb^{3+}. With regard to the stabilization of the 1:2 complexes, the entropic terms seem to be preponderant with La^{3+} and Yb^{3+} ($T\Delta S_2 = T\Delta S_{12} - T\Delta S_{11} = 18$ kJ mol^{-1} for both cations), whereas the formation of the Eu^{3+} complex is characterized by a favourable enthalpic term ($-\Delta H_2 = 36$ kJ mol^{-1}).

Conclusions and Outlook

The compounds described here represent the first examples of molecules bearing combinations of hydrophobic anionic groups of type $\mathbf{A}^{(-)}$ and specific chelating functions for trivalent lanthanides and actinides **B** in geometrically predefined manner. The combination of the two groups on a calix[4]arene platform affords extractants with strongly increased extraction efficiencies for europium and americium from acidic aqueous phases. Distribution coefficients of more than 100 for a 10^{-5} M solution are clearly unprecedented and substantially higher than those reported previously for the covalent combination of one $\mathbf{A}^{(-)}$ with one **B** group.[19] Comparison of isomeric derivatives in the *cone* and *1,3-alternate* conformations shows that the four groups must be attached to the same side of the molecule. Modification of the spacer length for the CMPO groups (with constant spacer of the Cosan groups) suggests that the distances from the platform must be similar to allow a cooperative action.

Surprisingly, a similar cooperative effect is observed when the same concentration of CMPO/Cosan groups is offered by a 1:1 mixture of the tetrasubstituted calix[4]arenes **13** and **14**. This strongly suggests that the extraction occurs through the action of a dimeric species, which may be formed by two molecules of **6c** or by **13** and **14**. It will be interesting to see whether the attachment of CMPO and Cosan functions in adjacent positions will lead to similar extraction results, and if a comparable synergistic effect will also exist for an equimolar mixture of a tri-CMPO-mono-Cosan and a mono-CMPO-tri-Cosan.

Calixarenes substituted by CMPO and Cosan groups are therefore not only interesting as novel extractants for the treatment of nuclear wastes (for the preconcentration of trace amounts of these nuclides or as sensors for Ln/Ac, for instance). They also offer some challenging questions with respect to the extracting species and the extraction mechanism.

Experimental Section

The starting nitrile-substituted *t*Bu-calix[4]arenes **3a** and **3c–f** were prepared by reported procedures.[25] The caesium salt of cobalt bis(dicarbollide) and cobalt bis(dicarbollide)-dioxane [8-$O(CH_2CH_2)_2O^{(+)}$-1,2-$C_2B_9H_{10}$)-(1′,2′-$C_2B_9H_{11}$)-3,3′-Co][26] (**10**) were supplied by Katchem Ltd., Czech Republic. Solvents [i.e., THF, ethylene glycol dimethyl ether (DME)] were dried with sodium diphenyl ketyl and distilled prior to use. Toluene was dried with metallic sodium and distilled. Dry NaH of a large surface area (2.2 $m^2 g^{-1}$, 96%) was freshly prepared. All calixarenes were dried in vacuo for 8–12 h over P_2O_5 at 45 °C prior to use. Other chemicals were purchased from Aldrich, solvents from Aldrich, Lachema a.s. and Penta Ltd., Czech Republic, respectively, and were used without purification. Analytical TLC was carried out on Silufol® (silica gel on aluminium foil, starch as the binder, Kavalier, Czech Republic). Unless otherwise specified, column chromatography was performed on a high-purity silica gel (Merck Grade, Type 7754, 70–230 mesh, 60 Å), using acetonitrile/dichloromethane (1:3) as the mobile phase.

All reactions were performed with the use of standard vacuum or inert atmosphere techniques as described by Shriver,[27] although some operations, such as flash chromatography and crystallization were carried out in air. Melting points were determined in sealed capillaries on a Koefler stage and are uncorrected. As previously verified,[28,29] data for elemental analyses of organic calixarenes are often misleading, due to inclusion of solvent molecules, and cannot be considered appropriate criteria of purity. This effect is even more pronounced with the assumption of the bonding of anion **1** on such platforms and involvement of hydrated alkali metal cations in the structures. Nevertheless, the identities of the reported compounds were unambiguously established by their spectroscopic data.

The **^{1}H, ^{1}H{^{11}B}, ^{1}H{$^{11}B_{selective}$}, ^{1}H-^{1}H COSY, ^{11}B, ^{11}B{^{1}H} and ^{31}P{^{1}H} NMR spectra** were recorded on a Varian Mercury Plus 400 MHz spectrometer at 295 K in [D_6]acetone (frequencies 399.893 MHz for ^{1}H, 128.329 MHz for ^{11}B and 161.916 MHz for ^{31}P). The spectra of all amino derivatives **5a–f** were measured immediately after dissolution. All chemical shifts are given in ppm, ^{1}H signals are referenced to the residual proton signal of the deuterated solvent; ^{11}B and ^{31}P signals are referenced to $BF_3{\cdot}OEt_2$ and H_3PO_4 as external standards, respectively.

Analytical HPLC was used to check the purity. A Merck–Hitachi LaChrom HPLC system fitted with a DAD 7450 detector and an intelligent autosampler was used. Chromatographic procedure: an Ion-Pair RP chromatographic method with a binary gradient was used, based on the methods previously reported[20,30] for the separation of hydrophobic borate anions. Column: RP Separon SGX C8, 7 μm (silica with chemically bonded octyl groups) Tessek Prague, Chromatographic conditions: Solvent A: 6 mmol hexylamine acetate in 58% aqueous acetonitrile, solvent B: CH_3CN, linear gradient 12–25 min. until 50% solvent B (75% solvent B for all amino derivatives **5a–f** and protected amino derivatives **8a** and **8b**), then constant composition of the mobile phase until 40 min; flow rate 1 mL min^{-1}; detection DAD, fixed wavelengths 285, 295, 308 and 312 nm; sensitivity range 2 AUFS; samples of concentration approx. 1 mg mL^{-1} in the mobile phase or CH_3CN; the method allowed the resolution of most of the compounds from the real reaction mixtures and for the purity assay and control. Most of the non-calixarene compounds are eluted before the gradient starts.

Mass spectrometry was performed on a Bruker Esquire-LC Ion Trap instrument using Electrospray Ionization. Negative ions were detected. Samples dissolved in acetonitrile (concentrations 1 ng μL^{-1}) were introduced into the ion source by infusion of 3 μL min^{-1}, drying temperature was 300 °C, drying gas flow 5 L min^{-1}, nebulizing gas pressure 10 psi.

Extraction Tests: Extraction experiments were performed in polypropylene test tubes with polyethylene stoppers at laboratory temperature (25 ± 0.5 °C), using 1 mL of each phase. The samples were shaken for 1 h (10 min intervals were sufficient for attaining extraction equilibrium) on a rotating shaker. After shaking, the test tubes were centrifuged and 0.7 mL samples of each phase were taken for radioactivity measurement. All reagents and solvents used were of A.R. quality. The distribution of Eu and Am was studied using ^{152,154}Eu and ^{241}Am in trace amounts (radiochemical purity). The radioactivity of samples was measured with a single-channel γ analyser with NaI (Tl) well detector.

Determination of Complexation Thermodynamic Parameters

UV Absorption Spectrophotometry: The stability constants β, defined as the concentration ratios $[LnL_x^{3+}]/([Ln^{3+}][L]^x)$ (where Ln^{3+} is the lanthanide cation and L the ligand), were determined in methanol (Prolabo, Chromanorm, water content <0.1%) at 25 °C and constant ionic strength provided by 0.01 M Et_4NNO_3 (Acros) by UV absorption spectrophotometry according to the previously reported procedure.[31] The spectra were recorded on a Shimadzu UV-2101-PC spectrophotometer and the spectra were analysed by use of the Specfit program.[23] The ligand concentration was ca. 10^{-5} M and commercial hydrated lanthanum, europium and ytterbium nitrates (Alfa Aesar, 99.99%) were used as the Ln^{3+} salts, which were dried under vacuum at ambient temperature for at least 24 h. Their solutions were standardized by complexometry with EDTA and xylenol orange as coloured reagents.

Microcalorimetry: Microcalorimetric titrations were performed using the 2277 Thermal Activity Monitor microcalorimeter (Thermometric). Titrations were carried out at 25 °C with 2.7 mL of solutions of the ligand ($10^{-4} \le c_L \le 4 \times 10^{-4}$ M) in methanol using a 4 mL glass cell. The heats of formation of the complexes were measured after addition of 15 × 15 μL aliquots of $Ln(NO_3)_3$ (4–5×10^{-3} M) in the same solvent to the reaction cell. Chemical calibration was carried out by determination of the complexation enthalpy of the Ba^{2+} complex with [18]crown-6 in water or of the Rb^+ complex with [18]crown-6 in methanol, as recommended.[32] Corrections for the heat of dilution of the metal ion were determined in separate blank experiments without the ligand. An example of a thermogram is given in the electronic supporting information. The enthalpies of complexation and the stability constants of the complexes were refined simultaneously from these data by using the ligand-binding analysis program DIGITAM version 4.1[33] The entropies of complexation were derived from the expression $\Delta G = \Delta H - T\Delta S$.

Syntheses

Model compounds **12**, **13**[23] and **14**[13] were prepared by previously reported procedures. For the yields and physical properties of compounds **$Cs_2$4d**, **$Cs_2$4e**, **$Cs_2$4f**, **5d**, **5e**, **5f**, **$Na_2$6d**, **$Na_2$6e**, **$Na_2$6f** and **11** (i.e., their NMR characteristics, MS and other data) see the electronic supporting information.

General Method for the Synthesis of Calix[4]arenes (4a, 4c–f): The starting 1,3-bis(cyanoalkoxy)calix[4]arenes (**3a**, **3c–f**, 1.50 mmol) were stirred in mixtures of toluene (15 mL) and DME (5 mL) to dissolve the main portion of the calixarene (ca. 0.5–1 h). After that, NaH (95%, 3.1 mmol) was added and stirring was continued for 2 h. A solution of **10** (3.05 mmol) in toluene/DME (4:1, 20 mL) was then injected, and the reaction mixture was stirred at room temperature until the spot corresponding to **10** had disappeared on

TLC (10–48 h). The resulting solution was neutralized with a small amount of aqueous acetic acid (1 M) and the solvents were evaporated. The crude products were dissolved in Et_2O (25 mL) and washed twice with water. The organic layer was filtered to remove traces of the starting calixarene and the solvents were evaporated to dryness after the addition of water (10 mL). The orange precipitate was dissolved in water (10 mL) and aqueous ethanol, and then an excess of an aqueous solution of CsCl was added. The mixture was heated at reflux and the formed precipitate was filtered off, washed with 30% aqueous ethanol and dried in vacuo. The crude product was then dissolved in a mixture of CH_2Cl_2 (5–10 mL) and benzene (20 mL), and this solution was layered with hexane and left to crystallize for 2–3 d. The liquid phase was decanted and the resulting microcrystalline or semisolid material was dried. For compounds **4c**, the crystallization procedure was repeated three times. The **4c*** conformer could be obtained by evaporation of the mother liquors followed by threefold recrystallization from hot 70% aqueous ethanol. If necessary, a final purification was made by column chromatography.

$Cs_2$4a: Yield 2.07 g, (76%); R_f = 0.22 (C_2Cl_2/CH_3CN, 3:1); m.p. 213–214 °C. ^{1}H NMR (400 MHz, [D$_6$]acetone, 25 °C, TMS): δ = 7.31 (s, 4 H, ArH), 6.57 (s, 4 H, ArH), 5.27 (br. s, 4 H, OCH_2CN), 4.59 (d, $^2J_{H,H}$ = 13.2 Hz, 4 H, $ArCH_2Ar$, H_{ax}), 4.31, 4.26 (2 s, 8 H, cage CH), 4.01 (t, $^3J_{H,H}$ = 4.2 Hz, 8 H, CH_2O), 3.66 (t, $^3J_{H,H}$ = 5 Hz, 8 H, CH_2O), 3.32 (d, $^2J_{H,H}$ = 12.8 Hz, 4 H, $ArCH_2Ar$, H_{eq}), 1.36 (s, 18 H, *t*Bu), 0.85 (s, 18 H, *t*Bu) ppm. ^{11}B NMR (128 MHz, [D$_6$]acetone, 25 °C, $BF_3{\cdot}Et_2O$): δ = 23.0 (s, 1B; B8), 3.9 (d, $^1J_{B,H}$ = 142 Hz, 1B; B8′), 0.4 (d, $^1J_{B,H}$ = 140 Hz, 1B; B10′), –2.4 (d, $^1J_{B,H}$ = 142 Hz, 1B; B10), –4.3 (d, $^1J_{B,H}$ = 153 Hz, 2B; B4′,7′), –7.9, –8.1 (2 d, overlap, 6B; B4,7,9,12,9′,12′), –17.3 (d, $^1J_{B,H}$ = 146 Hz, 2B; B5′,11′), –20.5 (d, $^1J_{B,H}$ = 153 Hz, 2B; B5,11), –21.6 (d, $^1J_{B,H}$ = 173 Hz, 1B; B6′), –28.4 ppm (d, $^1J_{B,H}$ = 139 Hz, 1B; B6). MS (–54.9 V, ESI$^-$): *m*/*z* (%) = 773.2 (100), 776.1 (5) $[M]^{2-}$ (calcd. 776.0).

$Cs_2$4c: The precipitate of the Cs^+ salt was treated with hot aqueous 70% ethanol on a water bath at 80 °C, dissolved by addition of an excess of ethanol and left to crystallize overnight. The resulting microcrystalline orange precipitate was centrifuged off. Mother liquors, in which the *cone* conformer accumulated, were evaporated and recrystallized once again from aqueous ethanol. The mother solution was evaporated and crystallized twice from CH_2Cl_2/hexane. The solids were collected, dried and purified by column chromatography using CH_2Cl_2/CH_3CN, 1:3 as the mobile phase. The main side product, which accumulated in the crystalline mass after crystallization from ethanol, was identified as the *1,3-alternate* **$Cs_2$4c***.

$Cs_2$4c: Yield 700–840 mg; 25–30%; R_f = 0.27 (CH_2Cl_2/CH_3CN, 3:1); m.p. 175–178 °C. ^{1}H NMR (400 MHz, [D$_6$]acetone, 25 °C, TMS): δ = 7.22 (s, 4 H, ArH), 6.63 (s, 4 H, ArH), 4.39 (d, $^2J_{H,H}$ = 12.4 Hz, 4 H, $ArCH_2Ar$, H_{ax}), 4.30, 4.27 (2 s, 8 H, cage CH), 4.16 (t, $^3J_{H,H}$ = 7.6 Hz, 4 H, CH_2O), 3.98 (t, $^3J_{H,H}$ = 4.8 Hz, 4 H, CH_2O), 3.89 (t, $^3J_{H,H}$ = 5.2 Hz, 4 H, CH_2O), 3.67 (m, 8 H, CH_2O), 3.24 (d, $^2J_{H,H}$ = 12.8 Hz, 4 H, $ArCH_2Ar$, H_{eq}), 2.83 (t, $^3J_{H,H}$ = 7.2 Hz, 4 H, CH_2CN), 2.49 (m, 4 H, CH_2), 1.34 (s, 18 H, *t*Bu), 0.90 (s, 18 H, *t*Bu) ppm; B-H signals from $^1H\{^{11}B_{selective}\}$ NMR (400 MHz, [D$_6$]acetone, 25 °C, TMS): δ = 2.93 (H10′), 2.78 (H(4′,7′), 2.70 (H10), 2.41 (H8′), 2.94, 2.02, 1.80 (H 4,7,9,12,9′,12′) 1.68 (H5′,11′), 1.58 (H5,11), 1.44(H6′), 1.33 (H6) ppm. ^{11}B NMR (128 MHz, [D$_6$]acetone, 25 °C, $BF_3{\cdot}Et_2O$): δ = 23.0 (s, 1B; B8), 3.8 (d, $^1J_{B,H}$ = 142 Hz, 1B; B8′), 0.3 (d, $^1J_{B,H}$ = 139 Hz, 1B; B10′), –2.5 (d, $^1J_{B,H}$ = 142 Hz, 1B; B10), –4.5 (d, $^1J_{B,H}$ = 153 Hz, 2B; B4′,7′), –7.8, –8.2 (2 d, overlap, 6B; B4,7,9,12,9′,12′), –17.6 (d, $^1J_{B,H}$ = 146 Hz, 2B; B5′,11′), –20.7 (d, $^1J_{B,H}$ = 153 Hz, 2B; B5,11), –21.7 (d, $^1J_{B,H}$ = 173, Hz, 1B; B6′), –29.0 (d, $^1J_{B,H}$ = 139 Hz, 1B; B6) ppm. MS (–80 eV, ESI): *m*/*z* (%) = 801.6 (100), 804.6 (20) $[M]^{2-}$ (calcd. 804. 6).

$Cs_2$4c*: This compound was synthesized from **3c** (700 mg, 0.89 mmol) as described for **$Cs_2$4a** using Cs_2CO_3 (583 mg, 1.78 mmol) instead of NaH. The crude product was treated with 70% aqueous ethanol (25 mL) and dissolved completely upon addition of a small amount of ethanol, and left to crystallize overnight. The resulting microcrystalline orange precipitate was centrifuged off. This procedure was repeated twice. Final purification was made by column chromatography with CH_2Cl_2/CH_3CN, 1:3 as the mobile phase. Yield 810 mg (48%); R_f = 0.30 (CH_2Cl_2/CH_3CN, 3:1); m.p. 196–200 °C. ^{1}H NMR (400 MHz, [D$_6$]acetone, 25 °C, TMS): = 7.2 (s, 4 H, ArH), 7.17 (s, 4 H, ArH), 4.32, 4.30 (2 s, 8 H, cage CH), 4.0 (d, $^2J_{H,H}$ = 16.0 Hz, 4 H, $ArCH_2Ar$), 3.91 (d, $^2J_{H,H}$ = 16.8 Hz, 4 H, $ArCH_2Ar$), 3.79 (br. s, 4 H, CH_2O), 3.62 (t, $^3J_{H,H}$ = 6.8 Hz, 4 H, CH_2O), 3.56 (m, 8 H, CH_2O), 3.43 (t, $^3J_{H,H}$ = 4.8 Hz, 4 H, CH_2O), 3.01 (br. t, 4 H, CH_2CN), 2.11 (m, 4 H, CH_2), 1.36 (s, 18 H, *t*Bu), 1.35 (s, 18 H, *t*Bu) ppm; B-H signals from $^1H\{^{11}B_{selective}\}$ NMR (400 MHz, [D$_6$]acetone, 25 °C, TMS): δ = 2.94 (H10′), 2.79 (H(4′,7′), 2.71 (H10), 2.38 (H8′), 2.92, 1.99 (H 4,7,9,12,9′,12′) 1.69 (H5′,11′), 1.56 (H5,11), 1.37 (H6′), 1.21 (H6) ppm. ^{11}B NMR (128 MHz, [D$_6$]acetone, 25 °C, $BF_3{\cdot}Et_2O$): δ = 22.6 (s, 1B; B8), 3.3 (d, $^1J_{B,H}$ = 125 Hz, 1B; B8′), 0.4 (d, $^1J_{B,H}$ = 129 Hz, 1B; B10′), –2.4 (d, $^1J_{B,H}$ = 142 Hz, 1B; B10), –4.1 (d, $^1J_{B,H}$ = 153 Hz, 2B; B4′,7′), –7.9, –8.2 (2 d, overlap, 6B; B4,7,9,12,9′,12′), –17.3 (d, $^1J_{B,H}$ = 131 Hz, 2B; B5′,11′), –20.5 (d, $^1J_{B,H}$ = 144 Hz, 2B; B5,11), –21.7 (d, overlap, 1B; B6′), –28.5 (d, $^1J_{B,H}$ = 39 Hz, 1B; B6) ppm. MS (–70 V, ESI): *m*/*z* (%) = 801.5 (100), 804.6 (18) $[M]^{2-}$ (calcd. 804.6).

General Method for the Synthesis of Calix[4]arenes 5a and 5c–f: $Me_2S{\cdot}BH_3$ (2.0 mL) was added to a solution of **$Cs_2$4a** or **$Cs_2$4c–f** (0.5 mmol) in freshly distilled THF (30 mL). The reaction mixture was stirred for 3–7 d at ambient temperature (TLC monitoring, CH_2Cl_2/CH_3CN, 9:1). The reaction was then quenched by careful addition of ethanol (15 mL, dropwise) and water (5 mL), followed by HCl (3 M, 1 mL). Organic solvents were evaporated in vacuo and the products were extracted with Et_2O (3 20 mL). The ether extracts were washed with Na_2CO_3 (5%, 2 × 20 mL), brine (3 × 20 mL), HCl (3 M, 3 × 20 mL) and water (3 × 20 mL) and separated, and the solvents were evaporated to dryness at ambient temperature. The crude products were purified by flash chromatography with CH_2Cl_2/CH_3CN, 5:1 to 3:1 as the mobile phase and recrystallized from methanol.

Compound 5a: Yield 576 mg (74%); R_f = 0.75 (CH_2Cl_2/CH_3CN, 5:1); m.p. 231–233 °C. ^{1}H NMR (400 MHz, [D$_6$]acetone, 25 °C, TMS): δ = 8.3 (br. s, NH_3), 7.36 (s, 4 H, ArH), 6.73 (s, 4 H, ArH), 4.51 (br. d, 4 H, $ArCH_2Ar$, H_{ax}), 4.26 (br. t, 4 H, $OCH_2CH_2NH_3$), 4.05, 4.0 (2 s, 8 H, cage CH), 3.87 (br. t, 8 H, CH_2O), 3.67 (br. t, 8 H, CH_2O), 3.45 (br. t, 4 H, $OCH_2CH_2NH_3$), 3.42 (br. d, 4 H, $ArCH_2Ar$, H_{eq}), 1.38 (s, 18 H, *t*Bu), 0.9 ppm (s, 18 H, *t*Bu). ^{11}B NMR (128 MHz, [D$_6$]acetone, 25 °C, $BF_3{\cdot}Et_2O$): δ = 24.6 (s, 1B; B8), 4.4 (d, $^1J_{B,H}$ = 140 Hz, 1B; B8′), 0.4 (d, $^1J_{B,H}$ = 140 Hz, 1B; B10′), –2.4 (d, $^1J_{B,H}$ = 144 Hz, 1B; B10), –4.3 (d, $^1J_{B,H}$ = 151 Hz, 2B; B4′,7′), –8.0 (2 d, overlap, 6B; B4,7,9,12,9′,12′), –17.3 (d, $^1J_{B,H}$ = 145 Hz, 2B; B5′,11′), –20.5 (d, $^1J_{B,H}$ = 154 Hz, 2B; B5,11), –21.6 (d, overlap; B6′), –28.4 (d, $^1J_{B,H}$ = 140 Hz, 1B; B6) ppm. MS (–54.9 V, ESI$^-$): *m*/*z* (%) = 1557.2 (100), 1563.3 (15) $[M]^-$ (calcd. 1563.13).

Compound 5c: Yield 580 mg (72%); R_f = 0.81 (CH_2Cl_2/CH_3CN, 5:1); m.p. 244–248 °C. ^{1}H NMR (400 MHz, [D$_6$]acetone, 25 °C,

TMS): δ = 7.78 (br. s, NH_3), 6.88 (s, 4 H, ArH), 6.87 (s, 4 H, ArH), 4.47 (d, $^2J_{H,H}$ = 12.4 Hz, 4 H, $ArCH_2Ar$, H_{ax}), 4.26 (t, $^3J_{H,H}$ = 5.2 Hz, 4 H, CH_2O), 4.07 (s, 4 H, cage CH), 3.98 (m, 8 H, CH_2O), 3.91 (s, 4 H, cage CH), 3.79 (br. t, 4 H, CH_2O), 3.68 (br. t, 4 H, CH_2O), 3.46 (m, 4 H, CH_2N), 3.22 (d, $^2J_{H,H}$ = 12.4 Hz, 4 H, $ArCH_2Ar$, H_{eq}), 2.25 (m, 4 H, CH_2), 2.18 (m, 4 H, CH_2), 1.12 (s, 18 H, *t*Bu), 1.09 (s, 18 H, *t*Bu) ppm. ^{11}B NMR (128 MHz, [D$_6$]acetone, 25 °C, BF_3·Et_2O): δ = 24.7 (s, 1B; B8), 7.1 (d, $^1J_{B,H}$ = 142 Hz, 1B; B8′), 0.6 (br. d, $^1J_{B,H}$ = 139 Hz, 1B; B10′), –2.5 (d, $^1J_{B,H}$ = 142 Hz, 1B; B10), –5.6 (d, $^1J_{B,H}$ = 153 Hz, 2B; B4′,7′), –6.4, –9.2 (2 d, overlap, 6B; B4,7,9,12,9′,12′), –17.1 (d, $^1J_{B,H}$ = 146 Hz, 2B; B5′,11′), –19.9 (d, $^1J_{B,H}$ = 153 Hz, 2B; B5,11), –21.7 (br. d, 1B; B6′), –28.4 (d, $^1J_{B,H}$ = 139 Hz, 1B; B6) ppm. MS (–66 V, ESI$^-$): *m*/*z* (%) = 1610.9 (100) 1617.2 (8) [M – H]$^-$ (calcd. 1617.2).

Compound 5c*: Yield 555 mg (69%); R_f = 0.74 (CH_2Cl_2/CH_3CN, 5:1); m.p. 254–256 °C. ^{1}H NMR (400 MHz, [D$_6$]acetone, 25 °C, TMS): δ = 7.26 (s, 8 H, ArH), 4.26 (2 s, 8 H, cage CH), 4.03 (d, $^2J_{H,H}$ = 15.6 Hz, 4 H, $ArCH_2Ar$), 3.88 (d, $^2J_{H,H}$ = 15.6 Hz, 4 H, $ArCH_2Ar$), 3.82 (br. t, 4 H, CH_2O), 3.7 (t, $^3J_{H,H}$ = 5.2 Hz, 4 H, CH_2O), 3.61 (m, 4 H, CH_2O), 3.48 (t, $^3J_{H,H}$ = 5.0 Hz, 4 H, CH_2O), 3.36 (t, $J_{H,H}$ = 4.4 Hz, 4 H, CH_2O), 3.1 (br. s, 4 H, CH_2N), 1.89 (m, 8 H, CH_2), 1.34 (s, 18 H, *t*Bu), 1.33 (s, 18 H, *t*Bu) ppm; B-H signals from ^{1}H{$^{11}B_{selective}$} NMR (400 MHz, [D$_6$]acetone, 25 °C, TMS): δ = 2.93 (H10′), 2.78 (H(4′,7′), 2.73 (H10), 2.38 (H8′), 2.92, 1.99 (H 4,7,9,12,9′,12′) 1.69 (H5′,11′), 1.56 (H5,11), 1.37 (H6′), 1.25 (H6) ppm. ^{11}B NMR (128 MHz, [D$_6$]acetone, 25 °C, BF_3·Et_2O): δ = 23.6 (s, 1B; B8), 3.3 (d, $^1J_{B,H}$ = 125 Hz, 1B; B8′), 0.4 (d, $^1J_{B,H}$ = 129 Hz, 1B; B10′), –2.4 (d, $^1J_{B,H}$ = 142 Hz, 1B; B10), –4.1 (d, $^1J_{B,H}$ = 153 Hz, 2B; B4′,7′), –7.9, –8.2 (2 d, overlap, 6B; B4,7,9,12,9′,12′), –17.3 (d, $^1J_{B,H}$ = 131 Hz, 2B; B5′,11′), –20.5 (d, $^1J_{B,H}$ = 144 Hz, 2B; B5,11), –21.7 (d, overlap, 1B; B6′), –28.5 (d, $^1J_{B,H}$ = 139 Hz, 1B; B6) ppm. MS (–66 V, ESI$^-$): *m*/*z* (%) = 1611.9 (100), 1617.8 (12) [M – H]$^-$ (calcd. 1618).

Alternatively, compound **5c*** was obtained in an overall 14% yield by reduction of the evaporated and dried mother liquors from the first crystallization of Cs_2**4c**. The product was dissolved in hot benzene, cooled down, layered with hexane and left to crystallize for 3 d.

Compound 5b

a) Starting from the Phthalimido-Protected Calix[4]arene 7a: NaH (95%, 33 mg, 1.31 mmol) was added to a solution of calixarene **7a** (630 mg, 0.62 mmol) in toluene/DME (3:1, 20 mL). A solution of compound **10** (506 mg, 1.29 mmol) in the same solvent (15 mL) was then added dropwise by syringe and the reaction mixture was stirred at room temperature for 15 d. The reaction was quenched by addition of water (20 mL) and a few drops of acetic acid. After addition of ether (20 mL), the organic layer was separated and the aqueous phase was extracted by additional portions of ether (2 × 10 mL). The combined ether extracts were evaporated to dryness. The residue was purified by column chromatography starting with CH_2Cl_2/CH_3CN, 5:1 and gradually increasing the acetonitrile content to 3:1 to give compound **8a** (610 mg, 52%). For physical properties, ^{1}H and ^{11}B NMR and MS data see electronic supporting information.

Deprotection: Hydrazine hydrate (2 mL) was added to a solution of **8a** (600 mg, 0.32 mmol) in ethanol (20 mL). The reaction mixture was heated at reflux for 6 h and cooled down. Water (15 mL) was added, the ethanol was evaporated in vacuo, and the crude product was removed by suction. To remove the hydrazine associated with the product, the residue was dissolved in ether and washed with aqueous HCl (3 M, 2 × 20 mL), water (2 × 20 mL), NaOH (5%, 3 × 20 mL), water (2 × 20 mL), HCl (3 M, 3 × 20 mL) and finally with water (3 × 20 mL) to achieve neutrality. The ether layer was then evaporated to dryness to give the amino derivative **5b** (375 mg, 74%). R_f = 0.27 (CH_2Cl_2/CH_3CN, 3:1); m.p. 231–234 °C. ^{1}H NMR (400 MHz, [D$_6$]acetone, 25 °C, TMS): δ = 7.74 (br. s, 6 H, NH_3), 7.25 (s, 4 H, ArH), 6.76 (s, 4 H, ArH), 4.50 (d, $^2J_{H,H}$ = 12.0 Hz, 4 H, $ArCH_2Ar$, H_{ax}), 4.27 (br. s, 4 H, CH_2O), 4.11 (s, 4 H, cage CH), 4.06 (s, 4 H, cage CH), 3.96 (br. s, 8 H, CH_2O), 3.87 (br. s, 4 H, CH_2O), 3.79 (br. s, 4 H, CH_2O), 3.42–3.39 (m, 4 H, CH_2N), 3.29 (d, $^2J_{H,H}$ = 12.0 Hz, 4 H, $ArCH_2Ar$, H_{eq}), 2.58 (m, 4 H, CH_2), 1.32 (s, 18 H, *t*Bu), 0.94 ppm (s, 18 H, *t*Bu); B-H signals from ^{1}H{$^{11}B_{selective}$} NMR (400 MHz, [D$_6$]acetone, 25 °C, TMS): δ = 2.95 (H10′), 2.71 (H4′,7′), 2.70 (H10), 2.55 (H8′), 2.89, 2.12, 1.91 (H 4,7,9,12,9′,12′) 1.59 (H5′,11′), 1.57 (H5,11), 1.53 (H6′), 1.33 ppm (H6). ^{11}B NMR (128 MHz, [D$_6$]acetone, 25 °C, BF_3·Et_2O): δ = 24.7 (s, 1B; B8), 6.51 (d, $^1J_{B,H}$ = 146 Hz, 1B; B8′), 0.96 (d, $^1J_{B,H}$ = 143 Hz, 1B; B10′), –2.58 (d, $^1J_{B,H}$ = 164 Hz, 1B; B10), –6.3 (3 d, overlap, 8B; B4,7,4′,7′,9,12,9′,12′), –17.4 (d, $^1J_{B,H}$ = 152 Hz, 2B; B5′,11′), –20.1 (d, $^1J_{B,H}$ = 168 Hz, 2B; B5,11), –22.4 (d, $^1J_{B,H}$ = 162, Hz, 1B; B6′), –28.0 (d, $^1J_{B,H}$ = 158 Hz, 1B; B6) ppm. MS (–80 eV, ESI): *m*/*z* (%) = 1584.1 (100), 1590.1 (8) [M – H]$^-$, (calcd. 1590.2).

b) Starting from the BOC-Protected Calix[4]arene 7b: The calixarene **7b** (500 mg, 0.52 mmol) was deprotonated with NaH (25 mg, 104 mmol) in toluene/DME (3:1, 20 mL), and compound **10** (426 mg, 1.049 mmol) in the same solvent (20 mL) was then added. After stirring for 48 h, the reaction was quenched by addition of water (20 mL) and a few drops of acetic acid. Ether (20 mL) was added, the organic layer was separated, and the aqueous phase was extracted with diethyl ether (2 × 10 mL). The combined organic extracts were evaporated to dryness. The residue was purified by column chromatography starting with CH_2Cl_2/CH_3CN, 4:1 and gradually increasing the acetonitrile content to 1:3 to give compound **8b** (575 mg). Yield 61%; for physical properties, ^{1}H and ^{11}B NMR and MS data see Supporting Information.

Deprotection: TFA (50 mL) was added to a solution of protected derivative **8b** (550 mg, 0.31 mmol) in dichloromethane (50 mL) at 0 °C and the reaction mixture was stirred at this temperature for 2.5 h. The solution was washed with brine (100 mL), Na_2CO_3 (5%, 3 × 70 mL) and water (2 × 10 mL). The organic layer was separated and the solvents were evaporated. The product was dissolved in diethyl ether (25 mL) and washed with HCl (3 M, 2 × 20 mL), water (2 × 20 mL), NaOH (5%, 2 × 20 mL), water (2 × 20 mL), HCl (3 M, 3 × 20 mL) and water (3 × 20 mL) until neutrality was achieved. The ether layer was then evaporated to dryness to give the pure amino derivative **5b** 360 mg (75%); NMR spectra are reported above.

General Synthetic Procedure Leading to the Di-CMPO Derivatives $Na_2$6a–f: NaH (95%, 0.6 mmol) was added to the solution of one of the amino derivatives **5a**–**f** (0.3 mmol) in THF (20 mL), and the resulting slurry was stirred at room temperature for 2 h. Compound **9** (237 mg, 0.4 mmol) in THF (20 mL) was then added dropwise over 30 min, and the reaction mixture was stirred at room temperature for 12 h and then at 60 °C (3–8 h) until the TLC spot corresponding to the starting species had disappeared. After cooling down and standing overnight, sodium *p*-nitrophenolate, which precipitated from the solution, was isolated by filtration under nitrogen using a glass filter adapter. The solid was then washed with dry THF (2 × 5 mL). Ethanol (5 mL) was carefully added to the combined THF solutions, followed by water (15 mL) and several drops of HCl (3 M) to adjust the pH to approx. neutral. Solvents were removed under reduced pressure and the wet residue was dissolved in CH_2Cl_2 (30 mL) and washed twice with cold (0 °C) aque-

ous $NaHCO_3$ (5%, 50 mL) and with brine (5 × 20 mL). After addition of water (10 mL) the solvents were evaporated to dryness. The residue was recrystallized from CH_2Cl_2/isooctane. If necessary the products were additionally purified by repeated flash chromatography using CH_2Cl_2/acetonitrile (4:1 to 1:1) as mobile phase.

Compound $Na_2$6a: Yield 395 mg (63%); R_f = 0.52 (CH_2Cl_2/CH_3CN, 3:1); m.p. 238–242 °C. ^{1}H NMR (400 MHz, [D$_6$]acetone, 25 °C, TMS): δ = 7.94 (t, $^3J_{H,H}$ = 10.8 Hz, 8 H, PhH), 7.72 (br. t, 4 H, PhH), 7.72 (m, 8 H, PhH), 7.26 (s, 4 H, ArH), 6.57 (s, 4 H, ArH), 4.24 (d, $^2J_{H,H}$ = 12.4 Hz, 4 H, $ArCH_2Ar$, H_{ax}), 4.15 (s, 8 H, cage CH), 4.11 (d, $^2J_{P,H}$ = 11.6 Hz, 4 H, CH_2P), 4.02 (m, 4 H, CH_2O), 3.98 (m, 4 H, CH_2O), 3.87 (m, 4 H, CH_2O), 3.63 (m, 6 H, CH_2O), 3.59 (m, 4 H, CH_2O), 3.32 (d, $^2J_{H,H}$ = 12.0 Hz, 4 H, $ArCH_2Ar$, H_{eq}), 2.86 (m, 4 H, CH_2N), 1.38 (s, 18 H, *t*Bu), 0.85 ppm (s, 18 H, *t*Bu); ^{31}P{^{1}H} NMR (161.9 MHz, [D$_6$]acetone, 25 °C, H_3PO_4): δ = 38.6 ppm (s). ^{11}B NMR (128 MHz, [D$_6$]acetone, 25 °C, BF_3·Et_2O): δ = 24.4 (s, 1B; B8), 6.08 (d, $^1J_{B,H}$ = 142 Hz, 1B; B8′), 0.5 (d, $^1J_{B,H}$ = 139 Hz, 1B; B10′), –2.6 (d, $^1J_{B,H}$ = 142 Hz, 1B; B10), –5.3 (d, $^1J_{B,H}$ = 153 Hz, 2B; B4′,7′), –6.9 (2 d, overlap, 6B; B4,7,9,12,9′,12′), –17.3 (d, $^1J_{B,H}$ = 146 Hz, 2B; B5′,11′), –20.0 (d, $^1J_{B,H}$ = 153 Hz, 2B; B5,11), –21.6 (d, $^1J_{B,H}$ = 173, Hz, 1B; B6′), –28.5 ppm (d, $^1J_{B,H}$ = 139 Hz, 1B; B6). MS (–54.9 V, ESI$^-$): *m*/*z* (%) = 1018.1 (100) 1022.6 (12) $[M]^{2-}$ (calcd. 1022.6).

Compound $Na_2$6b: Yield 430 mg (68%); R_f = 0.67 (CH_2Cl_2/CH_3CN, 3:1); m.p. 276–282 °C (decomp.). ^{1}H NMR (400 MHz, [D$_6$]acetone, 25 °C, TMS): δ = 8.85 (br. s, NH), 7.92 (t, $^3J_{H,H}$ = 10 Hz, 8 H, PhH), 7.75 (m, 4 H, PhH), 7.67 (m, 8 H, PhH), 7.21 (s, 4 H, ArH), 6.61 (s, 4 H, ArH), 4.42 (d, $^2J_{H,H}$ = 12 Hz, 4 H, $ArCH_2Ar$, H_{ax}), 4.21 (s, 8 H, cage CH), 4.17 (br. t, 4 H, CH_2O), 4.02 (br. t, 4 H, CH_2O), 3.76 (d, $^2J_{P,H}$ = 12 Hz, 4 H, CH_2P), 3.68 (m, 4 H, CH_2O), 3.61 (br. s, 8 H, CH_2O), 3.39 (m, 4 H, CH_2N), 3.20 (br. s, 4 H, $ArCH_2Ar$, H_{eq}), 2.16 (m, 4 H, CH_2), 1.27 (s, 18 H, *t*Bu), 0.87 ppm (s, 18 H, *t*Bu); B-H signals from ^{1}H{$^{11}B_{selective}$} NMR (400 MHz, [D$_6$]acetone, 25 °C, TMS): δ = 2.94 (H10′), 2.74 (H(4′,7′), 2.71 (H10), 2.42 (H8′), 2.94, 1.97, 1.80 (H 4,7,9,12,9′,12′) 1.64 (H5′,11′), 1.58 (H5,11), 1.48 (H6′), 1.23 ppm (H6); ^{31}P{^{1}H} NMR (161.9 MHz, [D$_6$]acetone, 25 °C, H_3PO_4): δ = 34.9 ppm (s). ^{11}B NMR (128 MHz, [D$_6$]acetone, 25 °C, BF_3·Et_2O): δ = 23.8 (s, 1B; B8), 4.9 (d, $^1J_{B,H}$ = 144 Hz, 1B; B8′), 0.32 (d, $^1J_{B,H}$ = 127 Hz, 1B; B10′), –2.5 (d, $^1J_{B,H}$ = 147 Hz, 1B; B10), –4.4 (d, $^1J_{B,H}$ = 147 Hz, 2B; B4′,7′), –7.3 (2 d, overlap, 6B; B4,7,9,12,9′,12′), –17.4 (d, $^1J_{B,H}$ = 156 Hz, 2B; B5′,11′), –20.4 (d, $^1J_{B,H}$ = 159 Hz, 2B; B5,11), –22.0 (d, $^1J_{B,H}$ = 175, Hz, 1B; B6′), –28.3 ppm (d, $^1J_{B,H}$ = 139 Hz, 1B; B6). MS (–80 eV, ESI): *m*/*z* (%) = 1033.8 (100), 1036.7 (6) $[M]^{2-}$ (calcd. 1036.7).

Compound $Na_2$6c: Yield 570 mg (89%), R_f = 0.68 (CH_2Cl_2/CH_3CN, 3:1); m.p. 268–272 °C (decomp.). ^{1}H NMR (400 MHz, [D$_6$]acetone, 25 °C, TMS): δ = 7.92 (t, $^3J_{H,H}$ = 8 Hz, 8 H, PhH), 7.63 (t, $^3J_{H,H}$ = 8 Hz, 4 H, PhH), 7.54 (m, 4 H, ArH), 7.16 (s, 4 H, ArH), 6.62 (s, 4 H, PhH), 4.44 (d, $^2J_{H,H}$ = 12 Hz, 4 H, $ArCH_2Ar$, H_{ax}), 4.23, 4.21 (s, 8 H, cage CH), 3.95 (t, $^3J_{H,H}$ = 4 Hz, 4 H, CH_2O), 3.87 (br. t, 4 H, CH_2O), 3.78 (d, $^2J_{P,H}$ = 12 Hz, 4 H, CH_2P), 3.72 (m, 8 H, CH_2O), 3.59 (t, $^3J_{H,H}$ = 5 Hz, 4 H, CH_2O), 3.24 (br. q, 4 H, CH_2N), 3.17 (d, $^2J_{H,H}$ = 12 Hz, 4 H, $ArCH_2Ar$, H_{eq}), 1.95 (m, 4 H, CH_2), 1.64 (m, 4 H, CH_2), 1.31 (s, 18 H, *t*Bu), 0.91 ppm (s, 18 H, *t*Bu); ^{31}P{^{1}H} NMR (161.9 MHz, [D$_6$]acetone, 25 °C, H_3PO_4): δ = 34.7 ppm (s); B-H signals from ^{1}H{$^{11}B_{selective}$} NMR (400 MHz, [D$_6$]acetone, 25 °C, TMS): δ = 2.92 (H10′), 2.76 (H(4′,7′), 2.72 (H10), 2.44 (H8′), 2.94, 2.02, 1.80 (H 4,7,9,12,9′,12′) 1.68 (H5′,11′), 1.56 (H5,11), 1.48(H6′), 1.26 ppm (H6). ^{11}B NMR (128 MHz, [D$_6$]acetone, 25 °C, BF_3·Et_2O): δ = 23.5 (s, 1B; B8), 4.5 (d, $^1J_{B,H}$ = 142 Hz, 1B; B8′), 0.5 (d, $^1J_{B,H}$ = 139 Hz, 1B; B10′), –2.5 (d, $^1J_{B,H}$ = 145 Hz, 1B; B10), –4.4 (d, $^1J_{B,H}$ = 154 Hz, 2B; B4′,7′), –7.5 (2 d, overlap, 6B; B4,7,9,12,9′,12′), –17.3 (d, $^1J_{B,H}$ = 146 Hz, 2B; B5′,11′), –20.4 (d, $^1J_{B,H}$ = 163 Hz, 2B; B5,11), –21.6 (d, $^1J_{B,H}$ = 173, Hz, 1B; B6′), –28.4 ppm (d, $^1J_{B,H}$ = 139 Hz, 1B; B6). MS (–80 eV, ESI): *m*/*z* (%) = 2114.8 (100) 2121.8 (5) $[M + Na]^-$ (calcd. 2122).

Compound $Na_2$6c*: Yield 525 mg (82%), R_f = 0.62 (CH_2Cl_2/CH_3CN, 3:1); m.p. 271–274 °C. ^{1}H NMR (400 MHz, [D$_6$]acetone, 25 °C, TMS): δ = 7.88 (m, 8 H, PhH), 7.64 (t, $^3J_{H,H}$ = 7 Hz, 4 H, PhH), 7.53 (m, 8 H, ArH), 7.15 (s, 4 H, ArH), 6.98 (s, 4 H, ArH), 4.32, 4.29 (2 s, 8 H, cage CH), 3.93 (d, $^2J_{H,H}$ = 16 Hz, 4 H, $ArCH_2Ar$), 3.73 (d, $^2J_{H,H}$ = 16 Hz, 4 H, $ArCH_2Ar$), 3.63 (t, $^3J_{H,H}$ = 6 Hz, 4 H, CH_2O), 3.58 (d, ^2J(H,P) = 13 Hz, 4 H, CH_2P), 3.57 (t, $^3J_{H,H}$ = 5 Hz, 4 H, CH_2O), 3.45 (t, $^3J_{H,H}$ = 5 Hz, 4 H, CH_2O), 3.33 (t, $^3J_{H,H}$ = 6 Hz, 4 H, CH_2O), 3.16 (t, $^3J_{H,H}$ = 6 Hz, 4 H, CH_2O), 3.06 (br. q, 4 H, CH_2N), 1.79 (m, 4 H, CH_2), 1.59 (m, 4 H, CH_2), 1.36 (s, 18 H, *t*Bu), 1.23 ppm (s, 18 H, *t*Bu); ^{31}P{^{1}H} NMR (161.9 MHz, [D$_6$]acetone, 25 °C, H_3PO_4): δ = 30.27 ppm (s). ^{11}B NMR (128 MHz, [D$_6$]acetone, 25 °C, BF_3·Et_2O): δ = 22.6 (s, 1B; B8), 3.5 (d, $^1J_{B,H}$ = 144 Hz, 1B; B8′), 0.6 (d, $^1J_{B,H}$ = 141 Hz, 1B; B10′), –2.4 (d, $^1J_{B,H}$ = 140 Hz, 1B; B10), –4.0 (d, $^1J_{B,H}$ = 154 Hz, 2B; B4′,7′), –7.6 (2 d, overlap, 6B; B4,7,9,12,9′,12′), –17.3 (d, $^1J_{B,H}$ = 147 Hz, 2B; B5′,11′), –20.3 (d, $^1J_{B,H}$ = 152 Hz, 2B; B5,11), –21.6 (d, overlap 1B; B6′), –28.5 ppm (d, $^1J_{B,H}$ = 141 Hz, 1B; B6). MS (–80 eV, ESI): *m*/*z* (%) = 1047.1 (100), 1050.6 (8%) $[M]^{2-}$, 2115.8 (25), 2121.8 (2%) $[M + Na]^-$ (calcd. 2122).

Supporting Information (see also the footnote on the first page of this article): Experimental data for the synthesis of the longer-chain calixarenes **4d**–**f**, **5d**–**f**, **6d**–**f** and the phthalimido- and the Boc-protected amino calixarenes **8a** and **8b**, synthetic procedure for compound **11** and examples of microcalorimetric titrations of the ligands **6c** and **11**.

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