Cobalt Bis(dicarbollides)(1–) Covalently Attached to the Calix[4]arene Platform: The First Combination of Organic Bowl-Shaped Matrices and Inorganic Metallaborane Cluster Anions

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Various calix[4]arene and resorc[4]arene ionic compounds substituted by cobalt bis(dicarbollide) anions (**1**) have been prepared for the first time. From *t*Bu-calix[4]arene (**A**) the complete series of mono-, di-, tri- and tetrasubstituted derivatives bearing one to four cluster anions on the lower rim (**3**–**6**) have been obtained in the form of their alkali-metal salts by *O*-alkylation with the 1-dioxane derivative [8-O(CH_2-CH_2)$_2$O$^{(+)}$-1,2-$C_2B_9H_{10}$)-(1′,2′-$C_2B_9H_{11}$)-3,3′-Co] (**2**), all of which are *syn* or *cone* isomers. In contrast, disubstitution of the dipropyl ether of *t*Bu-calix[4]arene (**B**) led to a mixture of the *cone* and *1,3-alternate* conformers **7a** and **7b**, respectively. Starting from tetrapropoxy-calix[4]arene functionalised at the upper rim by carboxylic acid groups in distal positions (**C**) and an amino-bridged derivative [8,8′-μ-H_2N<(1,2-$C_2B_9H_{10}$)$_2$-3,3′-Co] (**8**), calix[4]arene **9**, disubstituted at the upper rim, was obtained as the main product along with the monosubstituted species **10**. Di- and tetrasubstituted ionic products (**11**–**15**) were also obtained from resorcarene-based cavitands by *O*-alkylation with the 1-dioxane derivative **2**. A pair of regioisomeric disubstitution products, **11a**,**b**, was isolated in the case of the hydroxy cavitand **D**, while **E**, functionalised by hydroxymethyl groups on the wide rim, and **F**, bearing hydroxy groups on the alkylidene bridges, gave the 1,3-di- (**12** and **14**) and the tetrasubstituted compounds (**13** and **15**), respectively. The molecular structure of the electroneutral dicaesium complex of the dianion **4** was determined by single-crystal X-ray diffraction analysis. The two Cs^+ cations are found in different coordination spheres in the structure of Cs_2**4**. Coordination of the Na^+ cation by the diethylene glycol chain and one calixarene lower rim oxygen atom was found in the crystal structure of the Na complex of the monoanion **3**.

Introduction

There is still a considerably growing interest in the use of calix[4]arenes[1,2] and the more rigid cavitands[3] derived from resorc[4]arene[4] as basic skeletons or platforms on which to assemble various functional groups in a well-defined arrangement in space. Numerous chemical modifications are available[5] at the upper (wide) rim or the lower (narrow) rim to fine tune their properties (e.g. solubility[6]) and their molecular shape.[1,2,7]

Examples of the use of calix[4]arenes or cavitands as molecular platforms extend from biologically relevant compounds[8] (glyco clusters,[9] de novo proteins,[10] antibody mimetics[11]) to enzyme mimics,[12] dendrimers,[13] scaffolds for dyes (e.g. porphyrin,[14] perylene[15]), building blocks for self-assembled capsules[16] or supramolecular ligands for metal–cation complexations, etc. Indeed, derivatives substituted with metal-binding groups at geometrically optimised sites have already proved to exhibit outstanding extraction properties for caesium,[17] strontium,[18] actinides and lanthanides from strongly acidic high level activity nuclear waste (HLW).[19] Their efficiency and selectivity is due to the incorporation of several (potentially different[20]) chelating groups on the lower and/or upper rim of the calixarene or cavitand[21] platform, where a pre-organized arrangement allows their cooperative action. The use of calixarenes

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and cavitands with organic functional groups in the partitioning of radionuclide cations from strongly acidic high level activity nuclear waste (HLW) is often accompanied by the unwanted co-transport of nitrate ions into the organic phase. Covalent bonding of cobalt bis(dicarbollide) anions to these platforms can, however, intermolecularly compensate the cationic charge of the radionuclide and thus reduce or eliminate the co-transport of nitrate ions.

The singly charged cobalt bis(dicarbollide)(1–)[22,23] ion $[(1,2\text{-}C_2B_9H_{11})\text{-}3\text{-}Co]^-$ (**1**) belongs to the class of electron-deficient, 12-vertex icosahedral borane clusters with 26 cage electrons, and are characterized by their extraordinary chemical and thermal stability and their similarity in properties to inorganic superacids.[23] These properties place them in the class of weakly coordinating or low nucleophilic anions[24] and make them suitable for stabilisation of transient complex cation particles in catalysis and for use as strong non-oxidizing acids,[25] solid electrolytes,[25] boron-rich carriers for Boron Neutron Capture Therapy (BNCT) of cancer treatment and diagnosis[25,26] and other applications.[25] Halogen derivatives of **1** were designed more than 25 years ago for the efficient extraction of $^{137}Cs^+$ and Sr^{2+} from highly acidic solutions.[25,27] This liquid–liquid extraction procedure developed into an industrial process currently called "UNEX".[28] Recently, new compounds of this class that incorporate multidentate ligands and are efficient in the extraction of trivalent α emitters have also been reported.[29,30]

Considering the partitioning of radionuclides from HLW, a positive synergistic effect of anion **1** on the extraction with modified calixarenes is often observed.[27] Creating novel anionic molecules based on calixarenes substituted with

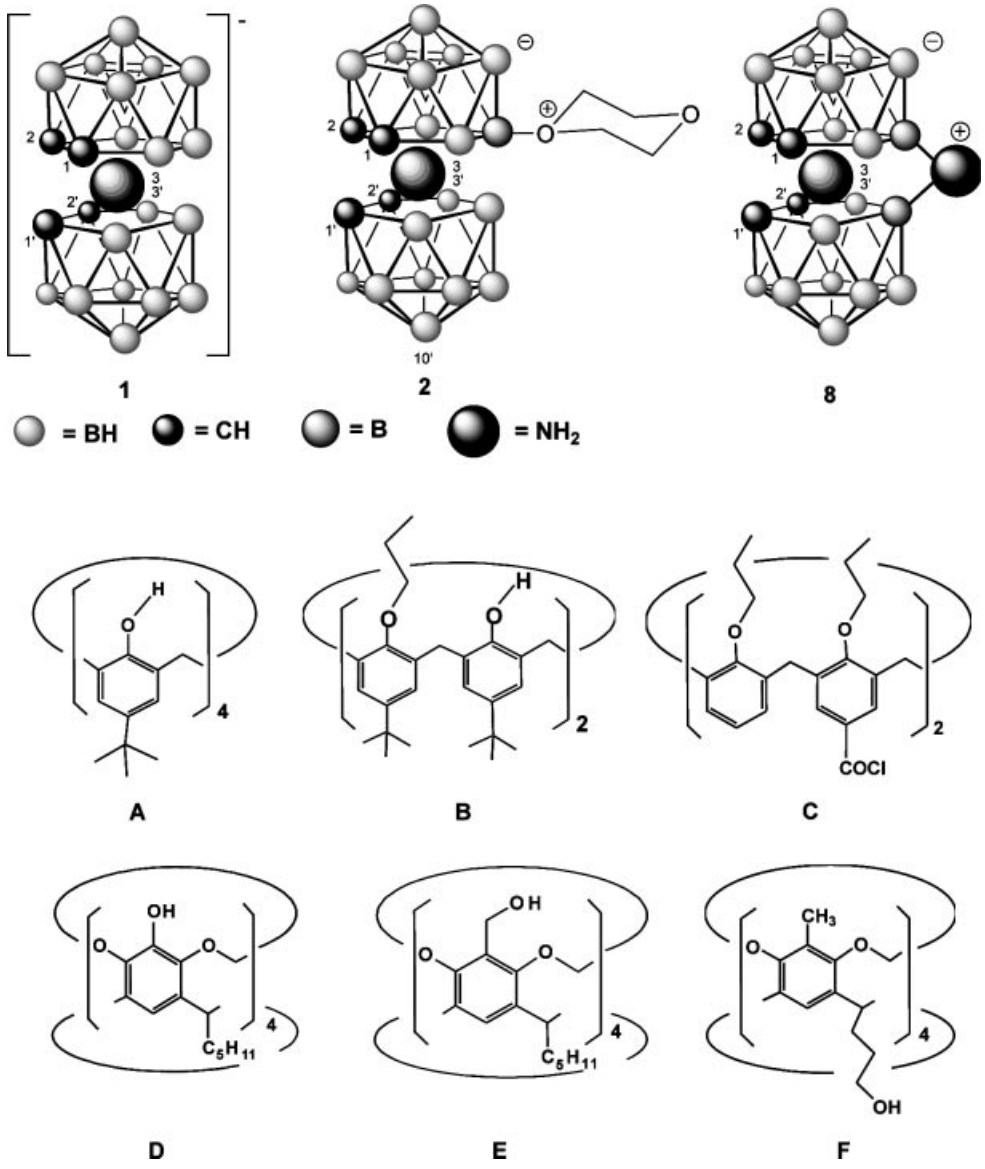


Figure 1. Schematic structures of the starting boron and calixarene compounds: cobalt bis(dicarbollide)(1–) ion **1**, cobalt bis(dicarbollide) dioxane derivative **2**, bridged amino derivative **8**, calix[4]arenes **A**–**C** and resorc[4]arene cavitands **D**–**F**.

hydrophobic (lipophilic) cluster anions is expected to provide qualitatively new properties that can improve the efficiency and stability of the whole extraction system. Calixarenes substituted by simple inorganic anionic[4,5,31] and organic ionic groups[1,4,5,20,32] have been reported, as well as examples of compounds substituted by metallocene moieties.[33] However, the issue of covalent linking of boron cluster compounds on the calixarene platforms has not been tackled to date. Only a few studies on inclusion complexes between the neutral *o*-carborane and the calix[5]arene[34] or *C*-methylresorc[4]arene cavitands[35] have brought together these two classes of interesting compounds.

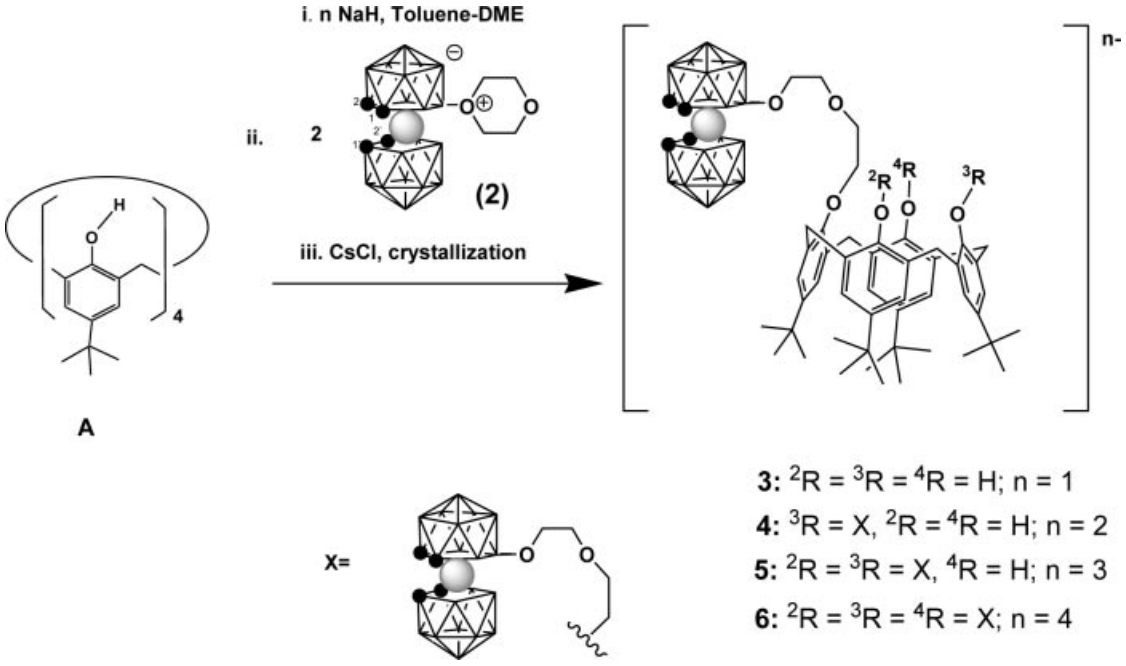
We present here a successful synthetic strategy leading to cobalt bis(dicarbollide) calix[4]arenes substituted at the lower rim of the cone conformation in good yields, along with examples of upper-rim-substituted calix[4]arenes and similar compounds from the resorc[4]arene cavitand series. The main objective of this first paper is to demonstrate the synthetic feasibility of binding hydrophobic cluster anions to particular supramolecular platforms through covalent bonds and to explore the scope and limitations of this approach with respect to a) lower and upper rim substitution, b) the number of anions which can be attached on a particular platform, and c) the stereochemistry of the reactions leading potentially to different conformers in the calix[4]arene series.

Results and Discussion

The synthetic methodology was mainly based on the metallaborate building block [8-O(CH_2CH_2)$_2$O-1,2-$C_2B_9H_{10}$)-($C_2B_9H_{11}$)-3,3′-Co] (**2**, Figure 1), a zwitterionic dioxane derivative of **1**[36] that has been used recently to attach the cluster **1** to various simpler organic molecules.[37,38] This reliable approach involves the cleavage of the oxonium ring of the derivative **2** by the nucleophilic attack of various reagents. For example, reactions with simple phenolates led smoothly to monovalent anions where the cluster of **1** is covalently bonded to the phenolic oxygen by an ethylene glycol spacer.[37] Considering the analogous sequential substitution by more than one anion **1** at the lower or upper rim of a calix[4]arene or resorc[4]arene cavitand, several questions arise. These are related to the gradual increase of the charge upon increasing the number of clusters of **1** on the platform (electrostatic repulsion), involvement of cation binding by transient particles and the steric demand provided by the bulky residues **1**. In principle, these factors can govern the solubility of particular species in the reaction media, the reaction rate and the product composition. The important points to be clarified are the regioselectivity of the attachment at both platforms (at their lower and upper rim), and the possibility of conformational changes in the case of the flexible calix[4]arene, which is prone to interconversion between the four general conformations (cone, partial cone, 1,2- and 1,3-alternate). Some confusing consequences of the above effects on the product isolation and characterization were observed in the course of preliminary studies, and the above points, in their whole complexity, had to be understood and clarified before the first pure products from this novel class of lipophilic anions could be obtained. The results are outlined below.

Substitutions at the Lower Rim of Calix[4]arenes

Several simple factors should be carefully controlled. The reactions are rather sensitive to any excess of the *t*Bu-calix[4]arene (**A**), the cobalt bis(dicarbollide) building block **2** and NaH (Scheme 1) and give complex mixtures of prod-



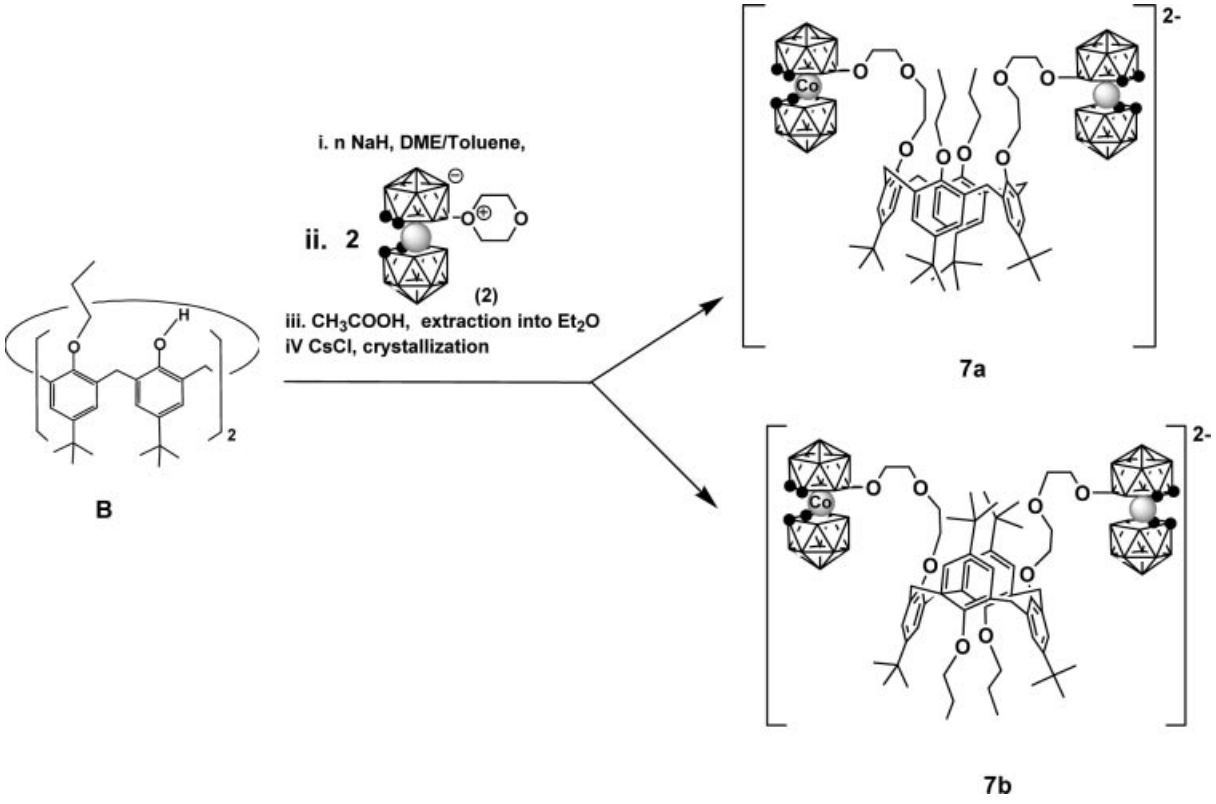
Scheme 1. General reaction scheme leading to derivatives **3**–**6**.

ucts in all these cases. NaH, which was found to be the best reagent for deprotonation, was used preferentially. In order to avoid the presence of other conformers, the reaction temperature should not exceed about 25 °C and the reaction should be carried out in a solvent of lower polarity than neat DME or THF, the best results being observed for toluene/ethylene glycol dimethyl ether (DME) mixtures. These reaction conditions led to clean substitutions of the *t*Bu-calix[4]arene platform and afforded the whole series of derivatives with one to four anionic residues at the lower rim (**3**–**6**).

Only compounds in the *syn* (or *cone*) conformation were isolated, and no sign of other conformers was found for either the sodium or caesium salts of these derivatives. The reaction with an **A/2** molar ratio of 1:2 gave a high yield of the 1,3-disubstituted derivative **4**, as would be expected for such bulky (and charged) substituents. No sign of formation of the 1,2-isomer, with two anionic residues in the adjacent calixarene sites, was observed. The crystal structure of the dicaesium salt of **4** (see crystallographic discussion below) shows the two Cs^+ ions in different positions. Apparently, corresponding to all our observations, this also has a stabilizing effect on the *syn* (*cone*) conformers in solution. The *syn* conformer of **4** was also isolated when Cs_2CO_3 was used instead of NaH under otherwise similar reaction conditions.

In light of the steric demands of the metallaborane moiety, it seemed unlikely to obtain *t*Bu-calix[4]arenes substituted at the lower rim with more than two anions **1**, as found, for instance, for the organic metallocene derivatives.[33] However, the tetrasubstituted derivative **6** in the *cone* conformation could be easily obtained in good yield provided that two equivalents of NaH and **2** were added to the solution of the disubstituted derivative **4** already generated in situ in a toluene/DME solvent mixture. Presumably, binding via a long and flexible spacer allows for such polysubstitution. The mono- and trisubstituted derivatives **3** and **5** were obtained, although in smaller yields, if the *t*Bu-calixarene was deprotonated with NaH and then treated with **2** in the respective stoichiometric amounts. In both cases, the disubstituted derivative **4** was formed in an appreciable quantity as the side product. This is further evidence for the preferential formation of **4**. An important factor for the efficient purification of **4** was the significantly lower solubility of its Cs^+ salt in aqueous ethanol or methanol with respect to the other products. Derivatives **3** and **5** could be isolated in pure form from the mother liquors remaining after removal of **4** by one or two fractional crystallizations. Flash chromatography, using either normal-phase or reverse-phase techniques, was used for the final purification of these compounds from the rest of the organic impurities. Analytical TLC and IP-RP-HPLC method (see Experimental Section) were used to follow the course of the reaction and to check the purity of the products. The molecular structure of the sodium salt of **3** was determined by X-ray diffraction analysis (see crystallographic discussion below).

In contrast to the above results, the reaction of **2** with the 1,3-dipropyl ether **B**, carried out under similar conditions in a 1:2 ratio, led to conformational changes of the calix[4]-



Scheme 2. Synthesis of stereoisomeric compounds **7a** and **7b** in the cone and 1,3-alternate conformations.

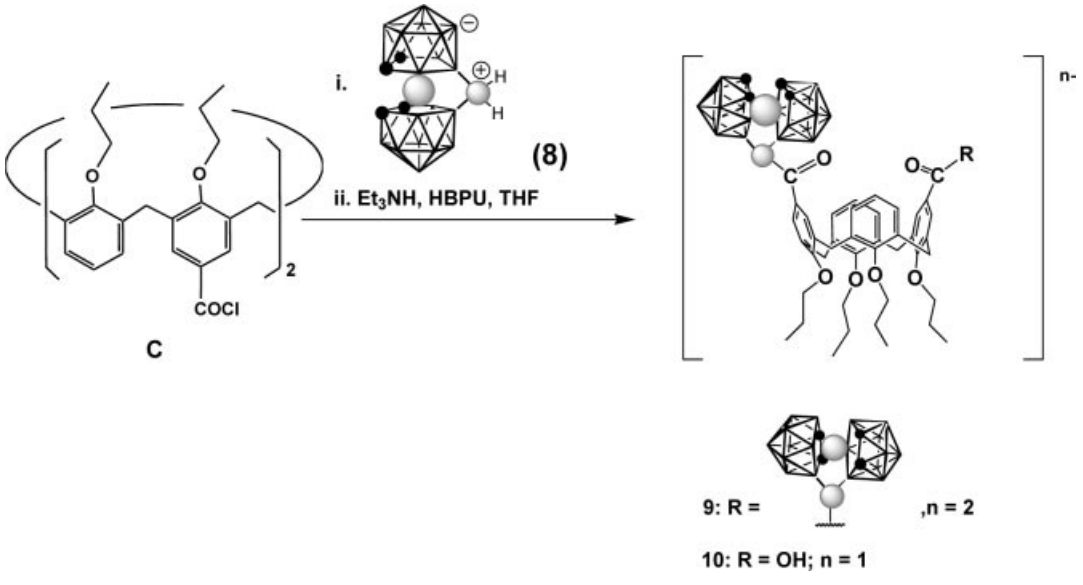
arene platform. The use of NaH for deprotonation of **B** in DME/toluene at room temperature or at 60 °C resulted in the formation of derivative **7** as a mixture of two conformers in a similar ratio close to 1:1, according to HPLC analysis and ^{11}B NMR spectroscopy [comparing the intensity of the two distinguishable singlets for B(8)]. Both species were isolated pure and in good yields of 28% and 33%, respectively, by fractional crystallization of their Cs^+ salts. The constitution of both conformers could be clearly established by ^1H and [^1H-^1H]-COSY NMR experiments as the *cone* (**7a**) and *1,3-alternate* conformers (**7b**; see the NMR discussion and Scheme 2). If Cs_2CO_3 was used as base, the conformer **7b** was obtained as the single calixarene product, but in much lower yield, only 18%, due to ring-opening side reactions of **2**. Considering that the starting compounds **B** and **4** differ only by the nature of the ether groups, it may be assumed that cation binding via O–M^+–O (from the ethylene glycol chain of **4**) interactions during the course of the reaction results in the stabilization of the *cone* conformation in **6**. If this type of cation bonding is weakened, the molecule tends to adopt the probably energetically more favourable *1,3-alternate* conformation of **7b** in order to minimize the steric strain.

Substitutions at the Upper Rim of Calix[4]arenes

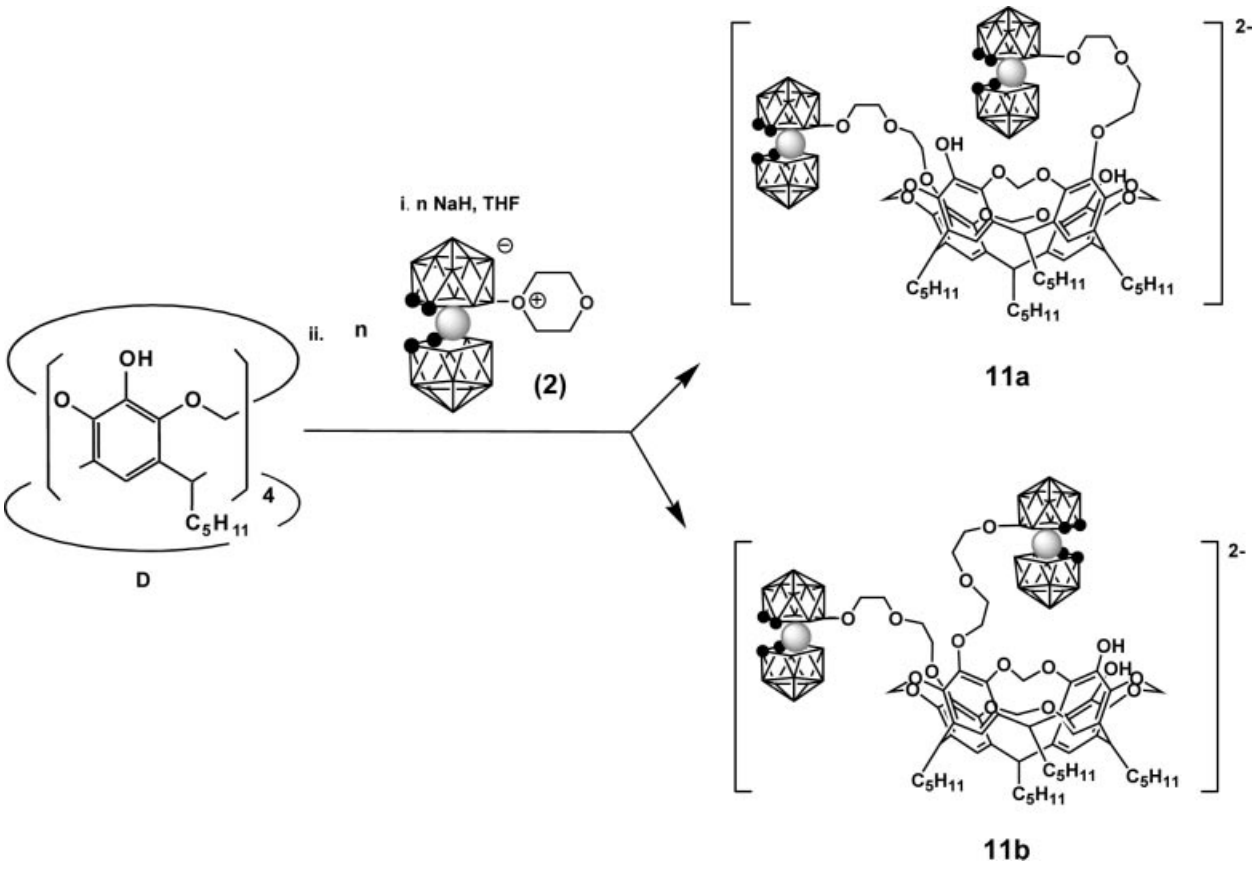
A different substitution scheme was applied to synthesize upper-rim-functionalized calix[4]arenes. Attachment of the cobalt bis(dicarbollide) moiety was achieved by formation of amide bonds starting from a conformationally fixed tetrapropyl ether 1,3-difunctionalized at the upper rim by carboxylic groups (**C**, see Figure 1), which were converted into acyl chloride groups prior to the reaction, using a known procedure.[39] The 1,3-dichloride **C** was treated with the bridged amino derivative [8,8′-H_2N<(1,2-$C_2B_9H_{10}$)$_2$-3,3′-Co][40] (**8**) after activation with HBPU (see Scheme 3). Coupling through amide bonds was achieved in moderate yield and the red main product was characterized as the disubstituted compound **9**. The monosubstituted product **10** was isolated in a smaller quantity from this reaction. Attempts to prepare the tetrasubstituted derivative starting from the respective tetraacid were not successful, leading instead to inseparable product mixtures. This can be rationalized in terms of the considerably higher steric demands of the rigid amino derivative in combination with the shorter connector arms.

Substitutions of Resorc[4]arene-Based Cavitands

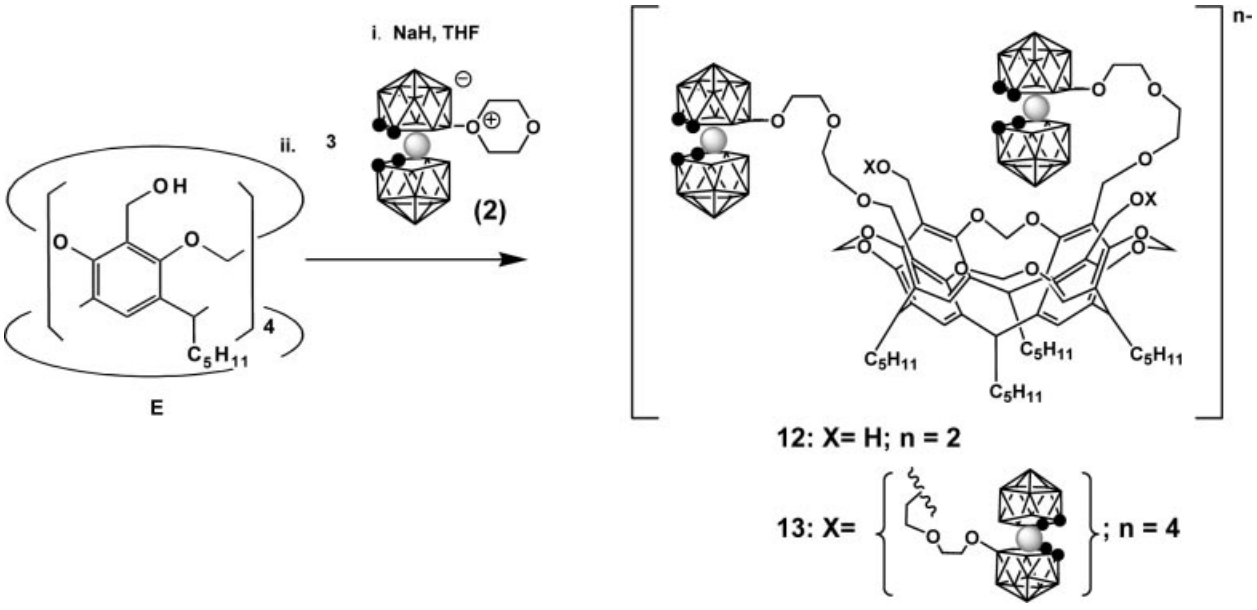
Reaction of the tetrahydroxycavitand **D** with 2.2 equivalents of **2** in the presence of excess NaH as a base in refluxing THF for 30 h gave a mixture of the 1,3- and 1,2-difunctionalised compounds **11a** and **11b**, respectively, in 42% yield (see Scheme 4). Successive chromatograph separations afforded the pure compounds as their disodium salts. From the reaction of the tetrakis(hydroxymethyl)cavitand **E** with three equivalents of **2** only the 1,3-disubstituted compound **12** and the tetrasubstituted derivative **13** were isolated in 27 and 5% yields, respectively (Scheme 5). Small amounts of the corresponding 1,2-difunctionalized product were detected in the crude reaction mixture by ^1H NMR spectroscopy and HPLC. Reaction of the lower-rim, hydroxypropyl-substituted cavitand **F** with 2.2 equivalents of **2** in the presence of 1.65 equivalents of NaH in THF at 45 °C for 30 h afforded the disubstituted product **14** as its disodium salt in 31% yield (Scheme 6). The corresponding reaction of cavitand **F** with four equivalents of **2** in the presence of NaH gave the tetrasubstituted compound **15** as the tetrasodium salt in 32% yield (Scheme 6). Cavitands containing a wider-diameter aperture and larger distances between binding sites are known to usually provide non-regioselective reaction pathways upon disubstitution,[3] and,



Scheme 3. Reaction procedure to the disubstituted (**9**) and monosubstituted (**10**) amides.



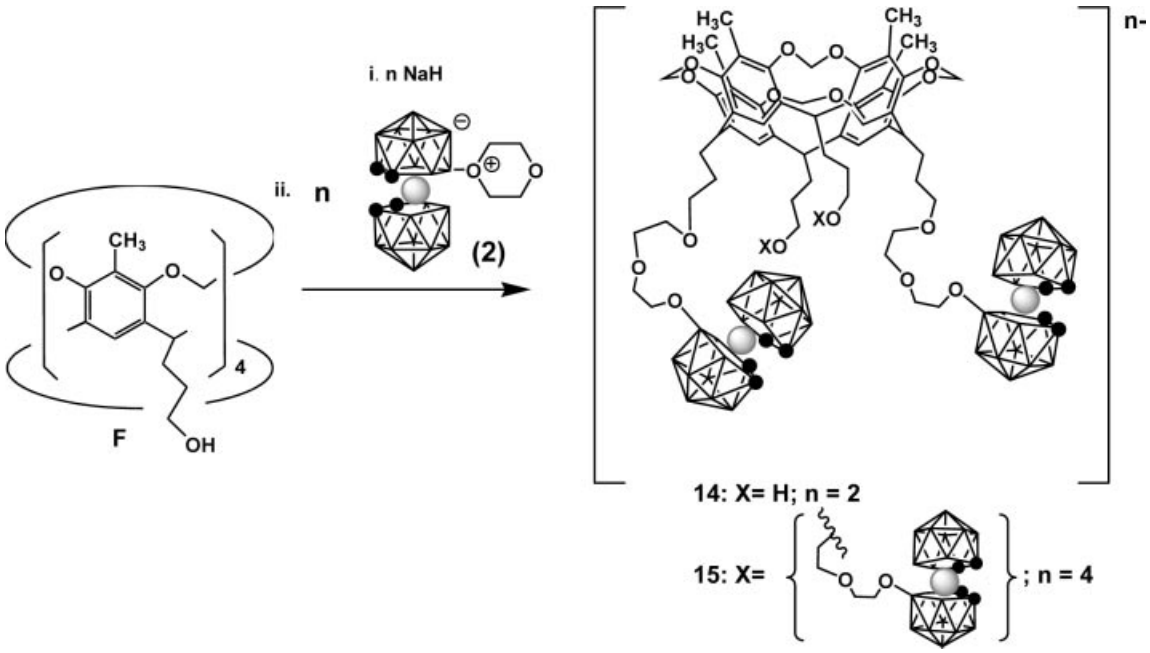
Scheme 4. Synthetic procedures to the two positional isomers of the disubstituted resorc[4]arene cavitands **11a** and **11b**.



Scheme 5. Synthesis of disubstituted and tetrasubstituted resorc[4]arene cavitands **12** and **13**.

as it seems from our observations, this rule is upheld, at least for cavitands **D** and **E**. The possibility to synthesize derivatives tetrasubstituted at either the upper or lower rim is exemplified by successful isolation of compounds **13** and **15**, which resulted from the respective reactions of the cavitands **E** and **F**.

An interesting property of all the above compounds **3**–**7** and **11**–**15** is their surprisingly good solubility in a broad series of solvents. The free conjugate acids are sparingly soluble in water, but readily soluble in organic solvents ranging from aqueous methanol to toluene. The solubility of the sodium salts is very similar, whereas the caesium salts are



Scheme 6. Synthesis of disubstituted and tetrasubstituted resorc[4]arene cavitands **14** and **15**.

slightly less soluble in low polarity solvents, especially chloroform, but still moderately soluble in CH_2Cl_2.

Spectral Properties of the Compounds

The ^{11}B NMR spectra of compounds **3**–**7** closely resemble the spectral pattern of the previously reported derivatives with simple phenol substituents[37] and the peak assignment was therefore made by analogy. There is no significant difference between the chemical shifts of the particular boron atom positions within this series, although some peak broadening and overlap is observed in the spectra of tri- and tetrasubstituted species for skeletal positions B(4,7) and B(9,9′,12,12′), as well as for B(5,11) and B(6′). In fact, the largest difference between chemical shifts was observed for the Cs^+ salt of **7b**, which shows an approximately 1 ppm downfield shift for the B(8) signal with respect to the Cs^+ salts of **7a** and all other compounds from this series. The B(8) singlets for the sodium salt of compound **4** appear about 0.6 ppm upfield from those of the caesium salt. Additionally, a small difference could be seen for particular H{^{11}B} proton positions in the selectively decoupled ^1H NMR spectra. The spectra of all resorc[4]arene derivatives **11**–**15** are also almost identical. A downfield shift (ca. 6 ppm) of the singlets corresponding to the boron atoms B(8,8′), can be seen in the ^{11}B NMR spectra of **9** and **10** in comparison with the peak of the parent compound (δ = 3.9 ppm). Only this signal is split into two peaks of equal intensity due to the asymmetric position of the bridge substituent with respect to the boron cage. The other peaks are almost unaffected by the substitution and exhibit a pseudo-symmetric pattern that is typical for the parent amino derivative and its simpler derivatives.[40] The main difference observed in the ^{11}B NMR spectra of di- and mono-substituted derivatives **9** and **10** is a considerable peak broadening in the spectrum of **9**, apparently due to averaging of slightly different signals of two boron cages attached in a more rigid manner than in the previous series.

The ^1H and ^{13}C NMR spectra of compounds **3**–**6** reflect the symmetry of their particular substitution pattern. The ratios of the intensities of the cage CH and CH_2O signals vs. the respective calix[4]arene signals in the ^1H NMR spectra are in agreement with the structures (see Figure 2). For example, the ^1H NMR spectrum of **4** exhibits two aromatic singlets of equal intensity, two $ArCH_2Ar$ doublets and two *t*Bu singlets along with four multiplets representative of the CH_2O moieties from the chain. The spectrum of the tetrasubstituted **6** reflects the C_{4v} symmetry of the molecule. For the sodium salt of the monosubstituted derivative **3**, four aromatic signals of equal intensity are found, two singlets and two m-coupled doublets due to the inequivalence of two of the Ar-H protons of the phenolic units adjacent to the *O*-alkylated unit. Three *t*Bu signals with intensities in the ratio 1:1:2 further confirm the (dynamic) C_s symmetry. A similar pattern is observed for the trisubstituted compound **5**, although with an opposite ratio of 1:3 for the intensities of calixarene vs. cage CH and OCH_2CH_2O signals. The spectral pattern of the cone conformer **7a** closely resembles that of the disubstituted compound **4** apart from the fact that the broader ArH signals almost coincide to one peak, and there are CH_2 and CH_3 signals from the propyl ether substituent. In contrast, two sharp ArH signals can be seen in the spectrum of the 1,3-alternate conformer **7b**, which are shifted downfield in comparison to **7a**. The main difference with respect to **7a** is the collapse of the two doublets of the methylene bridges from an AX system ($\Delta\delta$ = 1.21 ppm) into an AB system ($\Delta\delta$ = 0.13 ppm). This is in agreement with spectroscopic data reported for 1,3-alter-

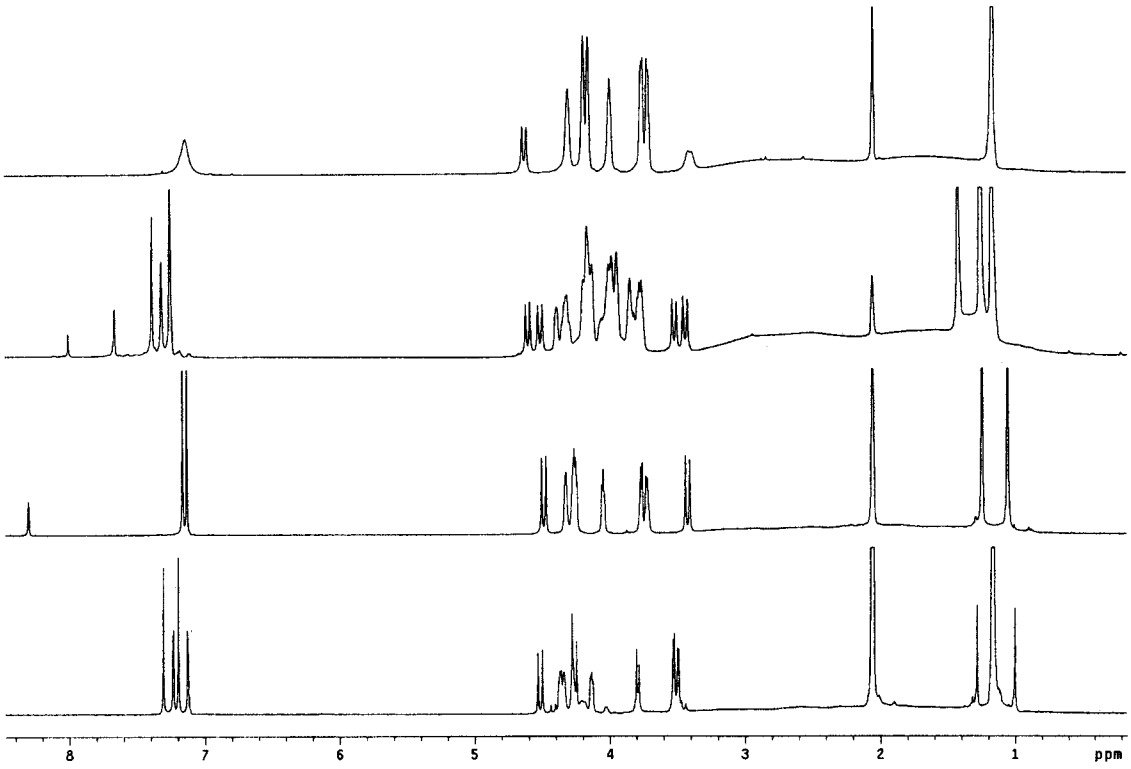


Figure 2. A plot of the ^{1}H NMR spectra (in deuterated acetone at 400 MHz) of compounds **3**–**6** (from bottom to top).

nate conformers in the literature.[1,2,41] The ^{1}H NMR spectrum of **9** has a typical pattern for 1,3-symmetrically substituted calix[4]arenes and closely resembles that reported for the starting dicarboxylic acid and its derivatives.[39] The main difference is the coincidental overlap of ArH signals of both phenolic units into one peak that integrates for eight protons, which is seen beside the triplet for two *p*-ArH. The spectra of **10** correspond to C_s symmetry.

The ^{1}H NMR spectra of the 1,3-disubstituted cavitands **11a** and **12** reflect their dynamic C_{2v} symmetry in solution, viz. two ArH signals, and two doublets for the OCH_2O cavitand bridges, although the higher field $ArOCH_2OAr$ signal for **11a** exhibits an additional splitting, possibly due to interactions with the boron cage. The ^{1}H NMR spectrum of the 1,2-substituted isomer **11b** shows, as expected, a pattern corresponding to C_s symmetry. The ^{1}H NMR spectra of both tetrasubstituted derivatives **13** and **15** are consistent with their C_{4v} symmetry as they exhibit only one aromatic signal and two $ArOCH_2OAr$ cavitand bridge doublets along with a triplet for the CHR bridge of the original resorcarene.

Electrospray mass spectrometry was used to characterise compounds **3**–**14** further. In most cases negative ions related to the molecular ion were observed with 100% abundance. The monosubstituted monoanions **3** and **10** exhibit a monocharged molecular ion M^-, while dianions, such as **4**, show M^{2-} peaks in all cases. For trianionic and tetraanionic species, signals for their alkali-metal complexes were usually observed as the respective base peaks, for example $[M + Na]^{2-}$ and $[M + Na]^{3-}$ for compounds **5** and **6**. The isotopic distribution in the boron plot of these peaks is in agreement with the charge, showing distances of 1, ½, and ⅓ mass units for mono-, di-, and trianionic compounds, respectively.

X-ray Structures of Cs_2**4** and Na**3**

The molecular structures of Cs_2**4** and Na**3** and their conformations deduced from the NMR spectra were unambiguously confirmed by single-crystal X-ray diffraction. They are shown in Figures 3 and 4, while selected bond lengths and angles are collected in Table 1.

In Cs_2**4** the calixarene assumes a pinched cone conformation with crystallographic C_2 symmetry. The angles between the central calixarene axis intersecting the two Cs^+ cations and the planes of aromatic rings substituted with diethylene glycol chains are 19.6°, while the aromatic rings with unsubstituted phenolic groups are inclined by 44.6°. Both anionic cages are oriented with their unsubstituted dicarbollide ligand parts closer to the calixarene cone and face towards the CH_2 bridges. The oxygens sitting at the boron atoms B(8) of the two dicarbollide ligands point towards each other and are coordinated to the caesium cation. The two boron cages are mutually inclined by 85.2°. The bond lengths and angles found in the two cages and the cluster geometries fall within the usual range found for simpler ethylene glycol substituted derivatives of anion **1**.[29,37] The position of the carbon atoms in these planes is staggered in both clusters, with identical torsion angles of

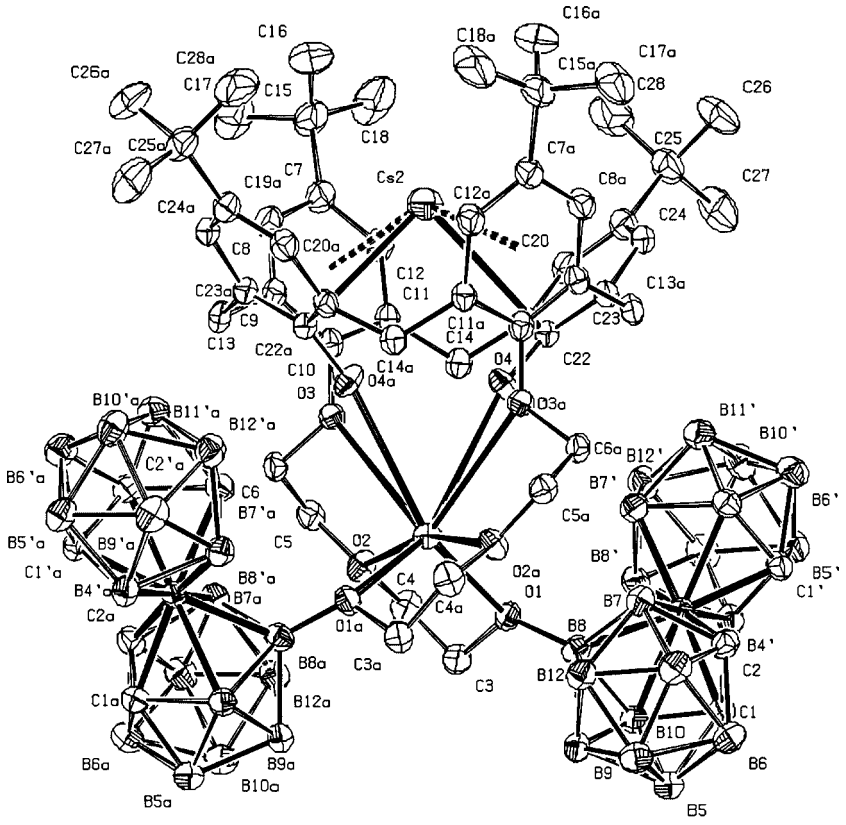


Figure 3. Lateral view of the X-ray crystal structure of Cs_2**4** with atom numbering scheme. Disordered water molecules and hydrogen atoms have been omitted for clarity. Only half of the atoms are symmetrically independent as the molecule exhibits a twofold axis of symmetry passing through Cs1 and Cs2. Displacement ellipsoids are drawn at the 30% probability level.

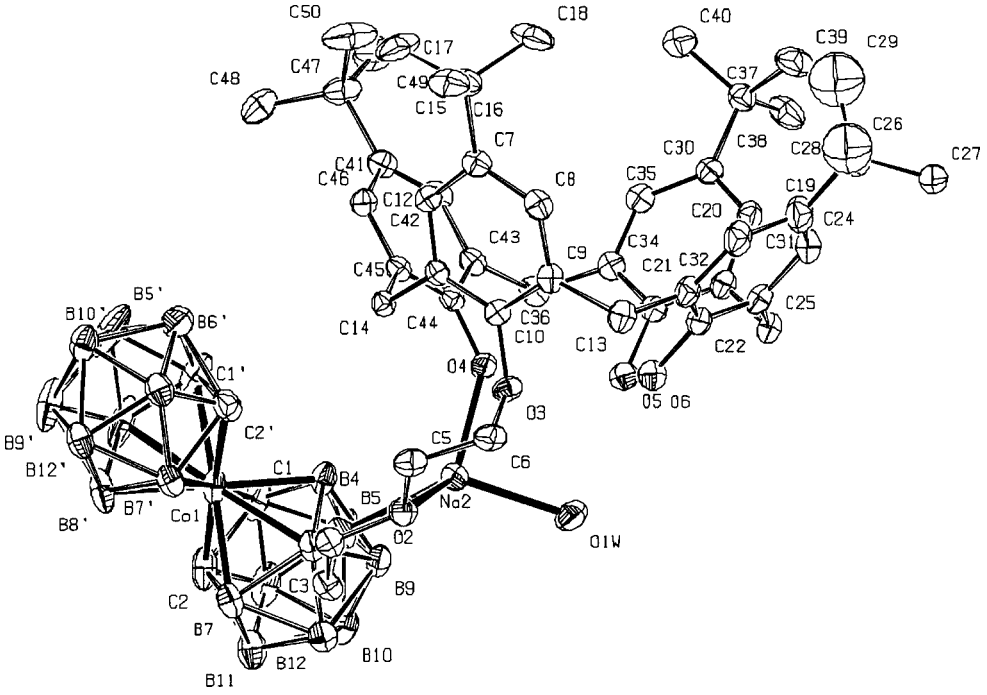


Figure 4. Lateral view of the X-ray crystal structure of Na**3** with atom numbering scheme. Disordered atoms of *t*Bu groups, CH_2Cl_2 solvent atoms, water molecules and hydrogen atoms have been omitted for clarity. Displacement ellipsoids are drawn at the 30% probability level.

Table 1. Selected geometrical parameters of Cs_2**4** and Na**3**.

Cs_2**4**		Na**3**	
Interatomic distances [Å]			
Cs(1)–O(1)	3.062(3)	Na(1)–O(1)	2.306(3)
Cs(1)–O(2)	3.176(2)	Na(1)–O(2)	2.366(3)
Cs(1)–O(3)	3.305(2)	Na(1)–O(3)	2.792(3)
Cs(1)–O(4)	3.140(2)	Na(1)–O(4)	2.272(3)
Cs(2)–C(7)	3.641(4)	Na(1)–O(1w)	2.256(4)
Cs(2)–C(19)	4.510(3)	C(22)–O(6)	1.390(5)
Cs(2)–C(10)	3.601(4)	C(44)–O(4)	1.375(5)
Cs(2)–C(22)	3.405(3)	C(14)–C(45)	1.520(5)
Cs(2)–O(1w)	3.471(5)	C(11)–C(14)	1.526(5)
O(3)–O(4)	3.235(4)	O(3)–O(4)	3.145(4)
O(4)–O(3^i)	2.643(4)	O(4)–O(5)	2.622(4)
O(1)–B(8)	1.426(2)	O(5)–O(6)	2.705(4)
O(1)–C(3)	1.407(5)	O(6)–O(3)	2.847(4)
H(O3)-H(O4)	1.678(8)	H(O4)–O(5)	1.719(5)
O(2)–C(5)	1.420(8)	H(O5)–O(6)	1.800(8)
O(2)–C(4)	1.425(2)	H(O6)–O(3)	1.913(1)
C(1)–C(2)	1.632(5)	C(1)–C(2)	1.625(7)
Angles [°]			
O(3)–Cs(1)–O(3^i)[a]	95.20(8)	O(1)–Na(1)–O(2)	71.1(1)
O(4)–Cs(1)–O(4^i)	61.1(1)	O(1)–Na(1)–O(4)	120.9(1)
O(2)–Cs(1)–O(2^i)	167.8(1)	O(1)–Na(1)–O(1w)	131.1(1)
O(1)–Cs(1)–O(1^i)	130.8(1)	O(2)–Na(1)–O(4)	134.6(1)
C(7)–Cs(2)–C(19)	82.41(8)	O(4)–Na(1)–O(1w)	88.2(1)
C(7)–Cs(2)–C(7^i)	169.4(1)	C(7)–Na(1)–C(19)	45.74(5)
C(19)–Cs(2)–C(19^i)	174.7(1)	C(9)–C(13)–C(21)	111.7(3)
Torsion angles [°]			
C(1)–C(2)–C(2′)–C(1′)	–39.5(3)	C(1)–C(2)–C(2′)–C(1′)	54.9(4)
C(19)–C(22)–C(22^i)-C(19^i)	–21.3(4)	C(19)–C(22)–C(44)–C(41)	–6.7(3)
C(7)–C(10)–C(10^i)-C(7^i)	19.0(3)	C(7)–C(10)–C(33)–C(30)	6.7(2)
C(7)–C(19)–C(7^i)–C(19^i)	11.8(1)	C(7)–C(19)–C(30)–C(42)	–14.47(8)
C(6)–C(10)–C(10^i)-C(6^i)	33.3(3)	O(2)–C(5)–C(6)–O(3)	69.3(4)
O(2)–O(3)–O(3^i)–O(2^i)	–48.9(2)		

[a] Symmetry code: (i) x, y, $1 - z$.

39.44°. The most interesting feature of the structure of Cs_2**4** is the ability of **4** to incorporate two Cs^+ cations at two distinctly different coordination sites. One Cs^+ cation is chelated by both diethylene glycol chains and is coordinated to two oxygen atoms of each spacer and to all four calixarene oxygen atoms (see Table 1 for details). Perhaps this coordination helps to keep the calixarene derivative in the *syn* conformation. The second Cs^+ cation is located inside the calixarene cavity at the upper rim of the molecule and its coordination sphere is completed by two additional water molecules. The distance of $Cs^+(2)$ from the centre of the aromatic rings is 3.344 Å for the rings bearing free phenolic groups and 3.740 Å for the two substituted with ethylene glycol chains. For comparison see a similar inclusion of Cs^+ into the cavity of *t*Bu-calix[4]arene.[42]

The molecular structure of the sodium salt of the monosubstituted derivative **3** was also determined. However, in this case disorder of the solvent molecules (CH_2Cl_2, H_2O) and of two *t*Bu groups of the calixarene prevented a good final refinement. On the other hand, the geometry of the metal binding site could be reliably determined. The Na^+ cation is coordinated outside the calix[4]arene cavity at the lower rim by two adjacent calixarene oxygen atoms (including the substituted one), two oxygen atoms from the diethylene glycol spacer, one water molecule and possibly also by a B(9)-H–Na bond. This kind of B(8′)-H–Na bonding has previously been observed in the structure of the simpler derivative **1**.[37] The position of the cluster carbon atoms in pentagonal planes of the dicarbollide ligands is staggered with a torsion angle of 54.9°, which is larger than in the previous case. The calixarene adopts an irregular pinched *cone* conformation, which is most probably stabilized by the three intramolecular O–H···O hydrogen bonds found in the structure. The inclination of the single aromatic units with respect to the normal on the reference plane, defined by the mean plane of the methylene carbons C13/C14/C25/C36, may be used to describe the conformation in more detail. Their values are 18.10° (C7–C12), 42.34° (C19–C24), 27.84° (C30–C35) and 35.57° (C41–C46). An interesting feature of the crystal packing in Na**3** is the formation of double layers consisting of calixarene molecules present in the *bc* plane. This plane is occupied by Na^+ cations and cobalt bis(dicarbollide) ions. The outer surface is sandwiched between the *t*Bu-calix[4]arene moieties with the *t*Bu groups pointing out of the double layer. The space between the double layers is filled with solvent molecules, one molecule of CH_2Cl_2 is

located in close proximity of each calixarene cavity, probably due to weak $C(CH_3)_3$–H···Cl interactions. However, the existence of such interactions could not be proved with certainty, due to only partial occupation of solvent positions and their disorder.

A comparison of the alkali metal binding sites in Cs_2**4** and Na**3** (Figures 2 and 3) suggests that the first alkali metal cation preferably occupies the position outside of the cavity and uses the oxygen donor atoms as binding sites. However, a deeper comparison should also consider the cations involved. Since the hard Na^+ cations prefer oxygen donors and the soft Cs^+ cations π-donors[17,43] a more profound argumentation can only be made on the basis of the crystal structures of Na_2**4** and Cs**3**, which are presently not available.

Conclusions

Efficient preparative routes have been developed for the covalent attachment of cobalt bis(dicarbollide) anions to various supramolecular platforms derived from calix[4]arenes. One to four anions of type **1** can be bound to the lower rim of *t*Bu-calix[4]arene when a diethylene glycol spacer is used, while a shorter amide link leads only to mono- and disubstitution even if effected at the upper rim. A strong influence of the particular calixarene derivatives and the reaction conditions on the stereochemistry of the resulting product and the product distribution has been demonstrated. Di- and tetrasubstitution by **1** was also achieved with cavitands derived from resorcarenes.

These novel anionic compounds combine the properties of basket-like molecules with those of hydrophobic, weakly coordinating anions of strong non-oxidizing inorganic acids. They could find applications as a new class of host molecules, as surfactants or as building blocks for the construction of more sophisticated, lipophilic ionic systems with interesting cation-binding properties. The study of their properties in liquid–liquid extraction of various cations from acidic solutions is in progress.

The synthetic procedures described here are the first step towards the construction of calixarene derivatives with mixed substitution, bearing anionic groups of type **1** in combination with specific chelating functions for trivalent lanthanides and actinides. The development of such extractants for the recovery of trivalent radionuclides from high level radioactive waste is one of the future goals.

Experimental Section

Commercially available *t*Bu-calix[4]arene was obtained from Aldrich; other calixarene samples were prepared according to the literature.[3,39] The caesium salt of cobalt bis(dicarbollide) was supplied by Katchem Ltd., Czech Republic. 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][36] (**2**) and [8,8′-μ-H_2N<(1,2-$C_2B_9H_{10})_2$-3,3′-Co])[40] (**8**) were prepared at the Institute of Inorganic Chemistry of the Academy of Sciences of the Czech Republic (I.I.C.) according to the described original procedures.

THF and ethylene glycol dimethyl ether (DME) were dried with sodium diphenyl ketyl and distilled before use. Toluene was dried with metallic sodium and distilled. Dry NaH with a large surface area (2.2 $m^2 g^{-1}$, 96%) prepared at I.I.C. was used throughout this work. All calixarene and cavitand chemicals were dried in vacuo for 8–12 h over P_2O_5 prior to use. Other chemicals and solvents were purchased from Aldrich, Lachema a.s. or Penta Ltd. (Czech Republic), and were used without purification. TLC was carried out on Silufol (silica gel on aluminium foil, Kavalier, Czech Republic), silica gel Merck 230–400 mesh, 60 Å, was used for column chromatography; an acetonitrile/dichloromethane (1:3) solvent mixture was used as the mobile phase unless otherwise specified.

All reactions were performed with the use of standard vacuum or inert-atmosphere techniques as described by Shriver,[44] 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 verified previously,[39,45] the data from elemental analyses of organic calixarenes are very often misleading due to inclusion of solvent molecules and cannot be considered as the appropriate criterion of purity. This effect is even more pronounced when taking into account the bonding of anion **1** to such platforms and the involvement of hydrated alkali metal cations in the structure. The identity of the reported compounds has been proven by their spectroscopic data.

^1H, $^1H\{^{11}B\}$, $^1H\{^{11}B$-*selective*$\}$, ^1H-^1H COSY, ^{11}B, $^{11}B\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectra were recorded on a Varian Mercury Plus 400 MHz spectrometer, in deuterioacetone (295 K) at 399.893 MHz for ^1H, 128.329 MHz for ^{11}B and 100.585 MHz for ^{13}C. All chemicals shifts are given in ppm and are referenced to the residual signal of the deuterated solvent.

Analytical HPLC: A Merck–Hitachi HPLC system equipped with a DAD detector and autosampler was used. Chromatographic procedure: An Ion-Pair RP chromatographic method with a binary gradient was used, based on the method for separation of hydrophobic borate anions described earlier in the literature.[46] Column: RP Separon Phenyl SGX 7 μm (silica with chemically bonded phenyl groups) Tessek, Prague; conditions: solvent A: 6 mmol hexylamine acetate in 58% aqueous acetonitrile, solvent B: CH_3CN, linear gradient from 12 min. to 25 min. until 50% of solvent B, then constant composition of the mobile phase until 40 min.; Flow rate 1 mL min^{-1}; detection: DAD at fixed wavelengths of 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; injection volume: 10 μL. HPLC k' values (capacity factors) of particular compounds were 16.5 (**3**), 15.5 (**4**), 14.4 (**5**), 13.7 (**6**), 16.6 (**7a**), 17.2 (**7b**), 17.0 (**11a**), 17.3 (**11b**), 15.03 (**12**), 14.9 (**13**), 14.6 (**14**) and 13.9 (**15**). Our method allowed for resolution of most of the compounds from the real reaction mixture and for purity assay and control. Most of the non-calixarene compounds were eluted before the gradient started. It can be seen that with an increased number of substituents the selectivity decreases; however, compounds **3**–**6**, **7a** and **7b** could be base-line resolved. Compounds **9** and **10** were analysed by a similar method on a Separon SGX C8 7 μm (spherical silica gel with chemically bonded octyl groups) column from Tessek, Prague. Chromatographic conditions were identical apart from solvent A (3 mmol hexylamine acetate in 58% aqueous acetonitrile). The respective k' values are 18.2 and 17.0 for compounds **9** and **10**.

Mass spectrometry measurements were performed on a Bruker Esquire-LC Ion Trap instrument by the electrospray ionization technique. Negative ions were detected. Samples dissolved in acetoni-

trile (concentrations 1 ng μL^{-1}) were introduced into the ion source by infusion at 3 μL min^{-1}; the drying temperature was 300 °C, the drying gas flow 5 L min^{-1} and the nebulizing gas pressure 10 psi.

X-ray Crystallography: The crystals for the X-ray diffraction study were grown by dissolving about 5 mg of Cs_2**4** or Na**3** in CH_2Cl_2 (0.5 mL) with addition of one drop of 80% aqueous ethanol. This solution was carefully over-layered with hexane and left to crystallize for two days. Orange octahedral crystals of Cs_2**4** and needles of Na**3** formed. Both crystals were mounted on a glass capillary with epoxy glue and measured on a Nonius KappaCCD diffractometer by monochromated Mo-K_α radiation (λ = 0.71073 Å) at 150(2) K. The structures were solved by direct methods (SIR92[47]) and refined by full-matrix least-squares techniques based on F^2 (SHELXL 97[48]). The hydrogen atoms of the hydroxyl moieties in Na**3** and Cs_2**4** were found on a difference Fourier map (the others were placed into idealised positions). All hydrogen atoms were fixed during refinement (riding model) with assigned temperature factors H_{iso}(H) = 1.2 U_{eq}(pivot atom) or 1.5 U_{eq} for methyl moiety in both structures.

Crystal Data for Na3: $C_{52}H_{84}B_{18}CoNaO_6{\cdot}2H_2O{\cdot}1.3CH_2Cl_2$, M = 1228.13, monoclinic, $P2_1/c$ (no 14), a = 18.3680(3) Å, b = 22.1120(2) Å, c = 17.8780(3) Å, β = 90.5770(6)°, V = 7260.84 Å^3, Z = 4, D_x = 1.122 Mg m^{-3}. Crystal dimensions 0.4 × 0.3 × 0.18 mm; absorption corrections were neglected (μ = 0.382 mm^{-1}); a total of 69 497 reflections were measured in the range h = –22 to 22, k = –23 to 26, l = –22 to 22 (θ_{max} = 26°), of which 14 208 were unique (R_{int} = 0.039) and 11 018 observed according to the $I > 2\sigma(I)$ criterion. Cell parameters were obtained from 13504 reflections (θ = 1–26°). The crystal suffers from disorder of solvent molecules and two *t*Bu moieties. Most of these atoms were refined isotropically using restrictions on geometry for these moieties. The hydrogens of the water molecules could not be resolved. The refinement converged (Δ/σ_{max} = 0.001) to R = 0.087 for observed reflections and wR = 0.295, GOF = 1.064 for 803 parameters and all 14 208 reflections. The final difference map displayed peaks in the vicinity of disordered solvents [$\Delta\rho_{max}$ = 1.873 e Å^{-3}), $\Delta\rho_{min}$ = –1.274 e Å^{-3}].

Crystal Data for $Cs_2$4: $C_{60}H_{112}B_{36}Co_2Cs_2O_8{\cdot}4H_2O$, M = 1806.4, tetragonal, $P4_32_12$ (no. 96), a = 19.5720(1) Å, c = 24.2560(1) Å, V = 9291.58(8) Å^3, Z = 4, D_x = 1.291 Mg m^{-3}. Red crystal of dimensions 0.3 × 0.3 × 0.22 mm. Absorption corrections were carried out using a multiscan procedure (PLATON) (μ = 1.178 mm^{-1}, T_{min} = 0.703, T_{max} = 0.750); a total of 160 558 reflections were measured in the range h = –25 to 25, k = –25 to 25, l = –31 to 31 (θ_{max} = 27.5°), of which 10 627 were unique (R_{int} = 0.055) and 9740 observed according to the $I > 2\sigma(I)$ criterion. Cell parameters were calculated from 108 073 reflections (θ = 1–27.5°). The oxygen atoms of the disordered water molecules were refined isotropically with partial occupation factors. As the crystal packing of the molecules leaves 14% of the unit cell volume accessible for solvent molecules, the position of solvent is not restricted and could not be resolved with high precision. The refinement converged (Δ/σ_{max} = 0.000) to R = 0.039 for observed reflections and wR = 0.109, GOF = 1.068 for 521 parameters and all 10 627 reflections. The final difference map displayed no peaks of chemical significance [$\Delta\rho_{max}$ = 0.918 e Å^{-3} (0.65 Å from solvent), $\Delta\rho_{min}$ = 1.537 e Å^{-3}, (0.73Å from Cs2). The absolute structure was assigned by reference to anomalous dispersion. (Flack parameter = –0.029(14)].

CCDC-246617 (for Na**3**) and -246618 (for Cs_2**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Caesium and Sodium Salts of 3: A solution of *t*Bu-calix[4]arene **A** (1.80 g, 2.77 mmol) in toluene/DME (4:1; 160 mL) was stirred with NaH (70 mg, 2.9 mmol) for 2 h. The reaction mixture was cooled down with ice and a solution of *closo-commo*-[(8-dioxane-1,2-$C_2B_9H_{10}$)(1′,2′-$C_2B_9H_{11}$)-3,3′-Co] **2** (1.14 g, 2.77 mmol) in toluene/DME (3:1, 20 mL) was added. The reaction was carried out as described in detail for compound **4** (see below) apart from the fact that the temperature was kept at 0 °C for the first 5 h. The resulting mixture was separated by repeated fractional crystallization followed by chromatography, as described for **4**. The monosubstituted product accumulated in the mother liquors. Yield of Cs**3**: 415 mg (11%). The second product, identified by HPLC and NMR spectroscopy as the disubstituted derivative **4**, was obtained in a yield of 1.28 g (31%). In another run, the Na^+ salts of **3** and **4** were directly separated from the crude product mixture by successive chromatography to yield 24% of Na**3** (based on **A**). Cs**3**: R_f = 0.61 (CH_2Cl_2/CH_3CN, 3:1). M.p. 190–192 °C; Na**3**: m.p. 185–187 °C. ^{1}H NMR (400 MHz, [D$_6$]acetone, 25 °C, TMS): δ = 9.90 (s, 1 H, OH), 9.15 (s, 2 H, OH), 7.32 (s, 2 H, ArH), 7.24 (d, $J_{H,H}$ = 2 Hz, 2 H, ArH), 7.26 (d, $J_{H,H}$ = 2 Hz, 2 H, ArH), 7.20 (s, 2 H, ArH), 7.13, 7.15 (2s, 2 H, ArH), 4.52 (d, $^2J_{H,H}$ = 13 Hz, 2 H, ArCH_2Ar, H_{ax}), 4.37 (m, 4 H, OCH_2CH_2O), 4.28 (m, 2 H, OCH_2CH_2O), 4.27 (d, $^2J_{H,H}$ = 14 Hz, 2 H, ArCH_2Ar, H_{ax}), 4.14 (m, 2 H, O-CH_2CH_2O), 3.81, 3.80 (s, 4 H, cage CH), 3.52 (d, $^2J_{H,H}$ = 13 Hz, 2 H, ArCH_2Ar, H_{eq}), 3.51 (d, $^2J_{H,H}$ = 13 Hz, 2 H, ArCH_2Ar, H_{eq}), 1.19 (s, 9 H, *t*Bu), 1.174 (s, 9 H, *t*Bu), 1.170 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′), 2.79 [H(4′,7′)], 2.71 (H10), 2.42 (H8′), 2.94, 2.02, 1.80 (H4,7,9,12,9′,12′) 1.68 (H5′,11′), 1.58 (H5,11), 1.41 (H6′), 1.23 ppm (H6). ^{11}B NMR (128 MHz, [D$_6$]acetone, 25 °C, $BF_3{\cdot}Et_2O$): δ = 22.9 (s, 1 B, B8), 3.8 (d, $^1J_{B,H}$ = 142 Hz, 1 B, B8′), 0.4 (d, $^1J_{B,H}$ = 139 Hz, 1 B, B10′), –2.4 (d, $^1J_{B,H}$ = 142 Hz, 1 B, B10), –4.2 (d, $^1J_{B,H}$ = 153 Hz, 2 B, B4′,7′), –7.4, –8.16 (d, $^1J_{B,H}$ = 139 Hz, 6 B, B4,7,9,12, 9′,12′), –17.3 (d, $^1J_{B,H}$ = 146 Hz, 2 B, B5′,11′), –20.4 (d, $^1J_{B,H}$ = 153 Hz, 2 B, B5,11), –21.57 (d, $^1J_{B,H}$ = 173 Hz, 1 B, B6′), –28.58 ppm (d, $^1J_{B,H}$ = 139 Hz, 1 B, B6). ^{13}C{^{1}H} NMR (101 MHz, [D$_6$]acetone, 25 °C, TMS): δ = 150.7, 149.2, 148.77, 148.76, 144.5, 143.9, 135.2, 129.4, 129.3, 128.8, 127.0, 126.5, 126.2 (ArC), 76.1 (CH$_2$O), 73.1 (CH$_2$O), 70.6 (CH$_2$O), 69.3 (CH$_2$O), 55.4 (cage CH), 47.3 (cage CH), 34.8, 34.5 (Ar-CH_2Ar), 32. 8, 31.3, (C, *t*Bu), 31.7, 31.5 ppm (CH$_3$, *t*Bu). MS (70 eV, ESI): m/z (%) = 1061.6 (100) [M]$^-$ (calcd. 1061.7).

Caesium Salt of 4: *t*Bu-calix[4]arene **A** (513 mg, 0.8 mmol) was dissolved in a mixture of toluene (10 mL) and ethylene glycol dimethyl ether (DME) (4 mL) in a 50-mL, two-necked Schlenk flask equipped with a nitrogen inlet and magnetic stirrer, which had been flushed with nitrogen. Once most of the calixarene had dissolved, NaH (38.6 mg, 1.6 mmol) was added with stirring. After 2 h a solution of **2** (651 mg, 1.6 mmol) in toluene/DME (8:1, 20 mL) was injected and the mixture was stirred overnight (12 h) at room temperature. The resulting solution was neutralised with a small amount of acetic acid/water (1:3) and the solvents evaporated. The crude product was dissolved in Et_2O (25 mL) and shaken three times with a 3 M solution of HCl (3 × 20 mL) and washed twice with water. The organic layer was filtered to remove a small amount of unreacted *t*Bu-calix[4]arene and evaporated almost to dryness after addition of water (10 mL). Water (10 mL) and aqueous ethanol were then added until the orange precipitate dissolved and then an excess of an aqueous solution of CsCl was added. The flask was put in a water bath and heated to reflux. The precipitate was dissolved by addition of ethanol and the contents of the flask were left to crystallize overnight. The resulting microcrystalline orange precipitate was centrifuged and recrystallized once more from hot

aqueous ethanol. Final purification was performed by column chromatography on silica gel (column 25×2.5 cm i.d.) using a CH_2Cl_2/CH_3CN mixture (1:3) as the mobile phase. This last chromatographic step is, however, not essential, as the product can be obtained in pure form after repeated crystallization. The main side product which accumulates in the mother liquors was identified as the trisubstituted derivative Cs_3**5** (see below) by NMR spectroscopy and was isolated as a minor product in a quantity of 250 mg (14%) after evaporation of the mother liquors and chromatography of the residue. Yield of Cs_2**4**: 920 mg (64%).

A reaction where Cs_2CO_3 was used instead of NaH for the deprotonation was carried out under otherwise identical reaction conditions in toluene/DME (3:7). A solution of **A** (0.26 g, 0.4 mmol) in toluene/DME (1:1, 20 mL) was deprotonated with Cs_2CO_3 (2.61 g, 0.8 mmol). Then, **2** (0.329 g, 0.8 mmol) was added to the solution, and the reaction was allowed to run for 20 h till the disappearance of **2** was detected by TLC. No removal of sodium by HCl was necessary in this case. The HPLC analysis showed a single peak corresponding to **4** and inspection of the NMR spectra proved its identity. Yield of Cs_2**4**: 0.327 g (56%).

$Cs_2$4: M.p. 298–300 °C. R_f = 0.58 (CH_2Cl_2/CH_3CN, 3:1). ^{1}H NMR (400 MHz, [D$_6$]acetone, 25 °C, TMS): δ = 7.81 (s, 2 H, OH), 7.20 (s, 4 H, ArH), 7.05 (s, 4 H, ArH), 4.43 (d, $^2J_{H,H}$ = 13 Hz, 4 H, $ArCH_2Ar$, H_{ax}), 4.27 (m, 4 H, OCH_2CH_2O), 4.25 (m, 8 H, OCH_2-CH_2O), 4.03 (m, 4 H, OCH_2CH_2O), 3.77 (s, 8 H, cage CH), 3.45 (d, $^2J_{H,H}$ = 13 Hz, 4 H, $ArCH_2Ar$, H_{eq}), 1.28 (s, 18 H, *t*Bu), 1.01 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 = 2.93 (H10′), 2.79 (H4′,7′), 2.7 (H10), 2.42 (H8′), 2.92, 2.02, 1.80 (H, 4,7,9,12,9′,12′) 1.67 (H5′,11′), 1.57 (H5,11), 1.41 (H6′), 1.25 ppm (H6). ^{11}B NMR (128 MHz, [D$_6$]acetone, 25 °C, $BF_3{\cdot}Et_2O$): δ = 23.5 (s, 2 B, B8), 4.8 (d, $^1J_{B,H}$ = 142 Hz, 2 B, B8′), 0.5 (d, $^1J_{B,H}$ = 139 Hz, 2 B, B10′), –2.5 (d, $^1J_{B,H}$ = 142 Hz, 2 B, B10), –4.5 (d, $^1J_{B,H}$ = 153 Hz, 4 B, B4′,7′), –7.6 (d, $^1J_{B,H}$ = 139 Hz, 12B, B4,7,9,12,9′,12′), –17.3 (d, $^1J_{B,H}$ = 146 Hz, 4 B, B5′,11′), –20.4 (d, $^1J_{B,H}$ = 153 Hz, 4 B, B5,11), –21.6 (d, $^1J_{B,H}$ = 173 Hz, 2 B, B6′), –28.6 ppm (d, $^1J_{B,H}$ = 139 Hz, 2 B, B6). ^{13}C{^{1}H} NMR (101 MHz, [D$_6$]acetone, 25 °C, TMS): δ = 151.4, 151.3, 147.8, 142.4, 133.9, 128.5, 126.7, 126.4 (ArC), 76.5 (CH_2O), 73.1 (CH_2O), 70.4 (CH_2O), 69.6 (CH_2O), 54.3 (cage CH), 47.5 (cage CH), 34.6 ($ArCH_2Ar$), 32.0 (C, *t*Bu), 31.4 ppm (CH_3, *t*Bu). MS (70 eV, ESI): *m/z* (%) = 736.8 (100) $[M]^{2-}$ (calcd. 737).

Caesium Salt of 5: A similar procedure was used as for Cs_2**4**, starting from calixarene **A** (1.027 g, 1.58 mmol), NaH (114 mg, 4.75 mmol) and **2** (1.95 g, 4.75 mmol). Toluene/DME (3:1) was used as solvent for the deprotonation of **A** (10 mL) and dissolution of **2** (20 mL). The crude product contained two species, which were separated by fractional crystallization, as described above for Cs**3** and Cs_2**4**. The less-soluble compound crystallizing out from the mixture of Cs^+ salts was identified as Cs_2**4** (1.01 g, 37%) according to HPLC and NMR spectroscopy. The more soluble product was the trisubstituted derivative Cs_3**5**, which was isolated as an orange powder in a yield of 1.88 g (52%) after final chromatographic purification.

$Cs_3$5: R_f = 0.27 (CH_2Cl_2/CH_3CN, 3:1); m.p. 245–247 °C. ^{1}H NMR (400 MHz, [D$_6$]acetone, 25 °C, TMS): δ = 8.10 (s, 1 H, OH), 7.37 (s, 2 H, ArH), 7.28 (d, 2 H, ArH), 7.20 (s, 2 H, ArH), 7.12 (d, 2 H, ArH), 4.61 (d, $^2J_{H,H}$ = 12 Hz, 2 H, $ArCH_2Ar$, H_{ax}), 4.52 (d, $^2J_{H,H}$ = 13 Hz, 2 H, $ArCH_2Ar$, H_{ax}), 4.50, 4.33 (m, 6 H, OCH_2-CH_2O), 4.17 (m, 12 H, OCH_2CH_2O), 4.01, 3.76 (m, 6 H, OCH_2-CH_2O), 3.95, 3.85 (2s, 4 H, cage CH), 3.52 (d, $^2J_{H,H}$ = 12 Hz, 2 H, $ArCH_2Ar$, H_{eq}), 3.44 (d, $^2J_{H,H}$ = 13 Hz, 2 H, $ArCH_2Ar$, H_{eq}), 1.85 (4 H, H_2O), 1.27 (s, 18 H, *t*Bu), 1.11 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 = 2.83 (H10′), 2.61 (H4′,7′), 2.71 (H10), 2.65 (H8′), 2.1, 1.86, 1.82 (H, 4,7,9,12,9′,12′) 1.64 (H5′,11′), 1.58 (H5,11), 1.41 (H6′), 1.23 ppm (H6). ^{11}B NMR (128 MHz, [D$_6$]acetone, 25 °C, $BF_3{\cdot}Et_2O$): δ = 23.6 (s, 3 B, B8), 5.0 (d, $^1J_{B,H}$ = 142 Hz, 3 B, B8′), 0.4 (d, $^1J_{B,H}$ = 139 Hz, 3 B, B10′), –2.2 (d, $^1J_{B,H}$ = 142 Hz, 3 B, B10), –4.7 (d, $^1J_{B,H}$ = 153 Hz, 6 B, B4′,7′), –7.3, –8.2 (d, $^1J_{B,H}$ = 139 Hz, 18B; B4,7,9,12,9′,12′), –17.3 (d, $^1J_{B,H}$ = 146 Hz, 6 B, B5′,11′), –20.3 (d, $^1J_{B,H}$ = 153 Hz, 6 B, B5,11), –21.6 (d, $^1J_{B,H}$ = 173 Hz, 3 B, B6′), –27.8 ppm (d, $^1J_{B,H}$ = 139 Hz, 3 B, B6). ^{13}C{^{1}H} NMR (101 MHz, [D$_6$]acetone, 25 °C, TMS): δ = 151.0, 151.6, 148.1, 144.5, 144.8, 136.3, 135.6, 134.5, 132.2, 132.0, 127.0, 126.8, 126.7, 126.3, 117.7 (ArC), 76.9, 75.9, 73.8, 73.5, 70.6, 70.0, 69.6, 69.3 (CH_2O), 54.2, 54.4 (cage CH), 47.7, 47.3 (cage CH), 34.8 ($ArCH_2Ar$), 34.6 ($ArCH_2Ar$), 32.3 (C, *t*Bu), 31.7 (CH_3, *t*Bu), 31.5 ppm (CH_3, *t*Bu). Na_3**5**: MS (70 eV, ESI): *m/z* (%) = 953.5 $[M + Na]^{2-}$ (100) (calcd. 954), 1931.2 (6) $[M + 2Na]^-$ (calcd. 1931).

Caesium Salt of 6: Similar conditions as described above for the disubstituted *t*Bu-calix[4]arene **4** were used, viz. 2.20 g (3.39 mmol) of parent calixarene **A**, 0.34 g (14.2 mmol) of NaH and 5.56 g (13.5 mmol) of **2**. However, the solution of **2** as well as NaH were added in two equal portions. The reaction mixture was stirred overnight after addition of the first portion to form the disubstituted compound Na_2**4** in situ. After the second half of NaH had been added to the reaction mixture, followed by 2 h stirring, the second part of a solution of **2** was added, and the stirring was continued for an additional 16 h. Pure compound Cs_4**6** (6.53 g, 68%) was obtained after twofold crystallization and chromatography on a 35×3.5 cm column using the same mobile phase as above, along with a smaller amount of disubstituted derivative Cs_2**4** (650 mg, 11%) and trisubstituted derivative Cs_3**5** (280 mg, 4%).

$Cs_4$6: R_f = 0.20 (CH_2Cl_2/CH_3CN, 3:1); m.p. 252–253 °C. ^{1}H NMR (400 MHz, [D$_6$]acetone, 25 °C, TMS): δ = 7.36 (s, 8 H, ArH), 4.69 (d, $^2J_{H,H}$ = 12 Hz, 4 H, $ArCH_2Ar$, H_{ax}), 4.38 (m, 8 H, OCH_2-CH_2O), 4.23 (s, 8 H, cage CH), 4.2 (s, 8 H, cage CH), 3.95 (m, 8 H, OCH_2CH_2O), 3.70 (m, 16 H, OCH_2CH_2O), 3.55 (d, $^2J_{H,H}$ = 12 Hz, 4 H, $ArCH_2Ar$, H_{eq}), 2.87 (s, 2 H, H_2O), 1.24 ppm (s, 36 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 (H4′,7′), 2.71 (H10), 2.56 (H8′), 2.91, 1.8 (H4,7,9,12,9′,12′) 1.66 (H5′,11′), 1.58 (H6′), 1.57 (H5,11), 1.23 ppm (H6). ^{11}B NMR (128 MHz, [D$_6$]acetone, 25 °C, $BF_3{\cdot}Et_2O$): δ = 23.4 (s, 4 B, B8), 4.4 (d, $^1J_{B,H}$ = 142 Hz, 4 B, B8′), 0.4 (d, $^1J_{B,H}$ = 136 Hz, 4 B, B10′), –2.5 (d, $^1J_{B,H}$ = 142 Hz, 4 B, B10), –4.5 (d, $^1J_{B,H}$ = 153 Hz, 8 B, B4′,7′), –7.7 (d, $^1J_{B,H}$ = 139 Hz, 16B, B9,12,9′,12′), –7.71 (d, $^1J_{B,H}$ = 142 Hz, 8 B, B4,7), –17.4 (d, $^1J_{B,H}$ = 146 Hz, 8 B, B5′,11′), –20.6 (d, $^1J_{B,H}$ = 153 Hz, 8 B, B5,11), –21.6 (d, $^1J_{B,H}$ = 173 Hz, 4B, B6′), –28.0 ppm (d, $^1J_{B,H}$ = 139 Hz, 4 B, B6). ^{13}C{^{1}H} NMR (101 MHz, [D$_6$]acetone, 25 °C, TMS): δ = 151.9, 150.9, 136.4, 126.9, 117.7 (ArC), 77.5 (CH_2O), 73.6 (CH_2O), 69.8 (CH_2O), 69.5 (CH_2O), 54.8 (cage CH), 47.4 (cage CH), 34.9 ($ArCH_2Ar$), 32.2 (C, *t*Bu), 31.6 ppm (CH_3, *t*Bu). MS (70 eV, ESI): *m/z* (%) = 773.1 (100) $[M + Na]^{3-}$ (calcd. 773.3), 1971.8 (25) $[M + 2Na]^{2-}$ (calcd. 1171.5).

Caesium Salts of 7a and 7b: A solution of *t*Bu-calix[4]arene dipropyl ether **B** (0.51 g, 1.25 mmol) in toluene/DME (4:1, 20 mL) was deprotonated by stirring with NaH (75 mg, 3.125 mmol) for 2 h. Then, a solution of **2** (1.02 g, 2.5 mmol) in toluene/DME (4:1, 16 mL) was added dropwise over 30 min. After 20 h the reaction was quenched by the addition of ethanol (2 mL) and a few drops of 1 M HCl. The crude product was isolated as described above for Cs_2**4**, and the resulting Cs^+ salts were purified (from organic species

and metallaborate side products) by flash chromatography on silica gel [column 25 × 2 cm; CH_3CN/CH_2Cl_2 (1:9 to 1:3) as eluent]. The main yellow-orange fraction consisted of two compounds according to HPLC analysis showing two singlets in the ^{11}B NMR spectrum for the substituted boron atom B(8) in a ratio of about 1: 1. They were separated by twofold crystallization from hot aqueous ethanol, as described for compounds **3**–**6**. While the 1,3-alternate conformer **7b** crystallized from the solution as a fine powder, which was collected by centrifugation, the cone conformer **7a**, identified by its ^1H NMR spectrum, accumulated in the mother liquors. Final purification of **7a** and **7b** by liquid chromatography, as described above for **3**, gave **7a** and **7b** in yields of 0.42 g (33%) and 0.36 g (28%), respectively. Treatment of **2** (0.27g, 0.66 mmol) with Cs_2CO_3 (0.21 g, 0.66 mmol) instead of NaH for the deprotonation of **B** (0.23 g 0.33 mmol) was carried out in DME under otherwise identical conditions. The reaction mixture was stirred for 5 d, until **2** disappeared (TLC detection). The appreciable quantities of cobaltacarborate species formed as side products were removed by flash chromatography on silica gel prior to crystallization of the calixarene-containing compound. HPLC analysis showed a single peak corresponding to **7b** as confirmed by the ^1H, ^{13}C and ^{11}B NMR spectra. Yield 90 mg (18%).

$Cs_2$7a: R_f = 0.35 (CH_3CN/CH_2Cl_2 1:3); m.p. > 360 °C. ^1H NMR (400 MHz, [D$_6$]acetone, 25 °C, TMS): δ = 7. 02 (br. s, 4 H, ArH), 6.91 (br. s, 4 H, ArH), 4.54 (d, $^2J_{H,H}$ = 12 Hz, 4 H, $ArCH_2Ar$, H_{ax}), 4.27 (br. t, 8 H, OCH_2CH_2O), 4.13 (br. t, 4 H, OCH_2CH_2O), 4.01 (t, 4 H, $^3J_{H,H}$ = 5 Hz, OCH_2CH_2O), 3.95 (t, $^3J_{H,H}$ = 5 Hz, 4 H, OCH_2CH_2O), 3.69 (s, 4 H, cage CH), 3.67 (s, 4 H, cage CH), 3.23 (br. d, $^2J_{H,H}$ = 11 Hz, 4 H, $ArCH_2Ar$, H_{eq}), 2.14 (m, 4 H, CH_2), 1.15 (s, 18 H, *t*Bu), 1.10 (s, 18 H, *t*Bu), 1.05 ppm (t, $^3J_{H,H}$ = 8 Hz, 6 H, CH_3); 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), 2.49 (H8′), 2.92, 2.03, 1.80 (H, 4,7,9,12,9′,12′) 1.66 (H5′,11′), 1.56 (H5,11), 1.30 (H6′), 1.12 ppm (H6). ^{11}B NMR (128 MHz, [D$_6$]acetone, 25 °C, $BF_3{\cdot}Et_2O$): δ = 22.98 (s, 2 B, B8), 4.0 (d, $^1J_{B,H}$ = 137 Hz, 2 B, B8′), 0.5 (d, $^1J_{B,H}$ = 137 Hz, 2 B, B10′), –2.5 (d, $^1J_{B,H}$ = 149 Hz, 2 B, B10), –4.1 (d, $^1J_{B,H}$ = 153 Hz, 4 B, B4′,7′), –7.4, –8.0 (d, $^1J_{B,H}$ = 139 Hz, 12B; B 4,7,9,12,9′,12′), –17.1 (d, $^1J_{B,H}$ = 146 Hz, 4B; B5′, 11′), –20.3 (d, $^1J_{B,H}$ = 153 Hz, 4 B, B5,11), –21.6 (d, $^1J_{B,H}$ = 173 Hz, 2 B, B6′), –28.3 ppm (d, $^1J_{B,H}$ = 139 Hz, 2 B, B6). $^{13}C\{^1H\}$ NMR (101 MHz, [D$_6$]acetone, 25 °C, TMS): δ = 153.6, 153.0, 146.4, 142.8, 135.1, 134.6, 126.1 (ArC), 77.7 (CH_2O), 72.8 (CH_2O), 71.1 (CH_2O), 69.52 (CH_2O), 66.8 (CH_2O), 54.9 (cage CH), 47.3 (cage CH), 34.5 ($ArCH_2Ar$), 33.6 (C, *t*Bu), 31.8 (CH_3, *t*Bu), 31.7 (CH_3, *t*Bu), 23.9 (CH_2), 10.7 ppm (CH_3). MS (70 eV, ESI): *m*/*z* (%) = 778.9 $[M]^{2-}$ (100) (calcd. 779), 1690.8 (18) $[M+Cs]^-$.

$Cs_2$7b: R_f = 0.33 (CH_3CN/CH_2Cl_2 1:3); m.p. 335–336 °C. ^1H NMR (400 MHz, [D$_6$]acetone, 25 °C, TMS): δ = 7.35 (s, 4 H, ArH), 7.22 (s, 4 H, ArH), 4.2 (br. s, 4 H, cage CH); 4.15 (br. s, 4 H, cage CH), 4.0 (d, $^2J_{H,H}$ = 16 Hz, 4 H, $ArCH_2Ar$), 3.91 (t, $^2J_{H,H}$ = 6 Hz, 4 H, OCH_2CH_2O), 3.87 (d, $^2J_{H,H}$ = 14 Hz, 4 H, $ArCH_2Ar$), 3.75 (br. t, 4 H, OCH_2CH_2O), 3.64 (t, $^3J_{H,H}$ = 5 Hz, 4 H, OCH_2CH_2O), 3.56 (m, 8 H, OCH_2CH_2O), 1.43 (m, 4 H, CH_2), 1.37 (s, 18 H, *t*Bu), 1.31 (s, 18 H, *t*Bu), 0.84 ppm (t, $^3J_{H,H}$ = 8 Hz, 6 H, CH_3); B-H signals from $^1H\{^{11}B$-*selective*$\}$ NMR (400 MHz, [D$_6$]acetone, 25 °C, TMS): δ = 2.94 (H10′), 2.72 (H10), 2.49 (H8′), 2.47 (H4′,7′), 2.93, 2.03, 1.80 (H4,7,9,12,9′,12′) 1.66 (H5′,11′), 1.59 (H5,11), 1.30 (H6′), 1.16 ppm (H6). ^{11}B NMR (128 MHz, [D$_6$]acetone, 25 °C, $BF_3.OEt_2$): δ = 23.6 (s, 2 B, B8), 5.1 (d, $^1J_{B,H}$ = 142 Hz, 2 B, B8′), 0.4 (d, $^1J_{B,H}$ = 139 Hz, 2 B, B10′), –2.6 (d, $^1J_{B,H}$ = 142 Hz, 2 B, B10), –4.47 (d, $^1J_{B,H}$ = 153 Hz, 4 B, B4′,7′), –7.2, –8.0 (d, $^1J_{B,H}$ = 139 Hz, 12B; B4,7,9,12,9′,12′), –17.3 (d, $^1J_{B,H}$ = 146 Hz, 4 B, B5′,11′), –20.2 (d, $^1J_{B,H}$ = 153 Hz, 4 B, B5,11), –21.6 (d, $^1J_{B,H}$ = 173 Hz, 2 B, B6′), –28.6 ppm (d, $^1J_{B,H}$ = 139 Hz, 2 B, B6). ^{13}C NMR (101 MHz, [D$_6$]acetone, 25 °C, TMS): δ = 156.5, 154.2, 146.1, 145.2, 137.1, 133.7, 128.3, 125.9 (ArC), 73.5 (CH_2O), 72.5 (CH_2O), 72.4 (CH_2O), 71.3 (CH_2O), 69.7 (CH_2O), 54.3 (cage CH), 47.3 (cage CH), 34.9 ($ArCH_2Ar$), 34.6 ($ArCH_2Ar$), 34.4 (C, *t*Bu), 32.1(CH_3, *t*Bu), 31.8 (CH_3, *t*Bu), 22.9 (CH_2), 10.8 ppm (CH_3). MS (70 eV, ESI) (%): *m*/*z* = 778.8 $[M]^{2-}$ (100) (calcd. 779), 1690.8 (7) $[M + Cs]^-$.

Sodium Salts of 9 and 10: Triethylamine (TEA; 0.5 mL, 3.6 mmol) and then a solution of diacyl chloride **C** (0.163 g, 0.227 mmol, prepared according to the described procedure[39]) in CH_2Cl_2 (50 mL) were added to a stirred solution of the bridged amino derivative [8,8′-μ-H_2N<(1,2-$C_2B_9H_{10})_2$-3,3′-Co] (**8**; 0.4 g, 1.18 mmol) in dichloromethane (70 mL) at 40 °C. After 30 min solid *O*-(benzotriazol-1-yl)-*N*,*N*,*N*′,*N*′-bis(pentamethylene)uronium tetrafluoroborate (HBPU; 0.105 g, 0.243 mmol) was added as coupling reagent, and after 5 h an additional amount of TEA (1 mL, 7.2 mmol). The reaction mixture was stirred for an additional 40 h, and then quenched by addition of 1 M hydrochloric acid (45 mL). The organic layer was separated, washed with a 5% solution of sodium hydrogen carbonate (3 × 20 mL) and water (2 × 10 mL), and the solvents evaporated to dryness. The crude product was purified by column chromatography (silica gel) using CH_2Cl_2 to elute the unreacted **8**, followed by CH_3CN/CH_2Cl_2 (1:3). Two fractions were collected (R_f = 0.73 and 0.15), containing the sodium salts Na_2**9** (0.105 g, 35%) and Na**10** (0.024 g, 8%), respectively.

$Na_2$9: R_f = 0.73 (CH_3CN/CH_2Cl_2, 1:3); m.p. > 360 °C. ^1H NMR (400 MHz, [D$_6$]acetone, 25 °C, TMS): δ = 6.85 (s, 8 H, ArH), 6.67 (br. t, 2 H, ArH), 4.61 (d, $^2J_{H,H}$ = 13 Hz, 4 H, $ArCH_2Ar$, H_{ax}), 3.99 (t, $^3J_{H,H}$ = 7 Hz, 4 H, OCH_2), 3.85 (t, $^3J_{H,H}$ = 7 Hz, 4 H, OCH_2), 3.39 (br. s, 8 H, cage CH), 3.23 (d, $^2J_{H,H}$ = 12 Hz, 4 H, $ArCH_2Ar$, H_{eq}), 2.91 (s, H_2O), 2.095 (q, 4 H, CH_2), 1.96 (q, 4 H, CH_2), 1.05 (t, $^3J_{H,H}$ = 8 Hz, 6 H, CH_3), 1.00 ppm (t, $^3J_{H,H}$ = 5 Hz, 8 H, CH_3); B-H signals from $^1H\{^{11}B$-*selective*$\}$ NMR (400 MHz, [D$_6$]acetone, 25 °C, TMS): δ = 2.9 (H10,10′), 2.80 (H4,7), 2.68 (H4′,7′), 1.65 (H9,9′,12,12′), 1.65, 1.15 (H5,5′,11,11′), 1.35 ppm (H6,6′). ^{11}B NMR (128 MHz, [D$_6$]acetone, 25 °C, $BF_3{\cdot}Et_2O$): δ = 10.2, 9.8 (2s, 4 B, B8,8′), –2.4 (br. d, 4 B, B10,10′), –6.3 (br. d, 4 B, B4,4′,7,7′), –9.4 (br. d, 8 B, B9,12,9′,12′), –16.1 (d, $^1J_{B,H}$ = 150 Hz, 8 B, B5, 5′,11,11′), –25.7 ppm (br. d, 4 B, B6,6′). $^{13}C\{^1H\}$ NMR (101 MHz, [D$_6$]acetone, 25 °C, TMS): δ = 173.1 (C=O), 157.0, 135.7, 134.7, 128.3, 129.6, 129.0, 123.7 (ArC), 77.6 (OCH_2), 77.2 (OCH_2), 43.1 (cage CH), 31.6 ($ArCH_2$ Ar), 23.8 (CH_2), 10.7 ppm (CH_3) ppm. MS (50 eV, ESI): *m*/*z* (%) = 1338.8 (3) [M + Na]$^-$, 660.1 (100) $[M]^{2-}$ (calcd. 659.4).

Na10: R_f = 0.15 (CH_3CN/CH_2Cl_2, 1:3); m.p. > 360 °C. ^1H NMR (400 MHz, [D$_6$]acetone, 25 °C, TMS): δ = 18.55 (s, 1 H, COOH), 7.95 (br. s, 1 H, NH), 7.79 (s, 2 H, ArH), 7.27 (s, 2 H, ArH), 6.29 (d, $^3J_{H,H}$ = 2 Hz, 2 H, ArH), 6.18 (t, 2 H, ArH), 6.11 (d, $^3J_{H,H}$ = 2 Hz, 2 H, ArH), 5.4 (br. s, NH), 4.52 (d, $^2J_{H,H}$ = 14 Hz, 2 H, $ArCH_2Ar$, H_{ax}), 4.43 (d, $^2J_{H,H}$ = 13 Hz, 2 H, $ArCH_2Ar$, H_{ax}), 4.16 (t, $^3J_{H,H}$ = 7 Hz, 2 H, O-CH_2), 4.04 (t, $^3J_{H,H}$ = 7 Hz, 2 H, OCH_2), 3.72 (m, 4 H, OCH_2), 3.39 (br. s, 4 H, cage CH), 3.25 (d, $^2J_{H,H}$ = 13 Hz, 2 H, $ArCH_2Ar$, H_{eq}), 3.16 (d, $^2J_{H,H}$ = 14 Hz, 2 H, $ArCH_2Ar$, H_{ax}), 2.88 (s, H_2O), 2.15 (m, 4 H, CH_2), 1.93 (m, 4 H, CH_2), 1.16 (t, $^3J_{H,H}$ = 8 Hz, 6 H, CH_3), 0.93 ppm (t, $^3J_{H,H}$ = 7 Hz, 6 H, CH_3); B-H signals from $^1H\{^{11}B$-*selective*$\}$ NMR (400 MHz, [D$_6$]acetone, 25 °C, TMS): δ = 2.88 (H10,10′), 2.80 (H4,7), 2.70 (H4′,7′), 2.10 (H9,9′,12,12′), 1.72, 1.15 (H5,5′,11,11′), 1.45 ppm (H6,6′). ^{11}B NMR (128 MHz, [D$_6$]acetone, 25 °C, $BF_3{\cdot}Et_2O$): δ = 10.0, 7.8 (2s, 2 B, B8,8′), –2.5 (d, 2 B, B10,10′), –6.44 (d, $^1J_{B,H}$ = 144 Hz, 4 B,

B4,7,4′,7′), –9.5 (d, $^1J_{B,H}$ = 125 Hz, 4 B, B9,12,9′,12′), –16.1 (d, $^1J_{B,H}$ = 150 Hz, 4 B, B5,5′,11,11′), –26.4 ppm (br. d, 1 B, B6,6′). ^{13}C NMR (101 MHz, [D$_6$]acetone, 25 °C, TMS): δ = 163.3 (C=O), 157.6 (C=O), 136.7, 133.6, 132.0, 130.3, 129.6, 127.9, 124.1 (ArC), 78.7 (OCH_2), 77.1 (OCH_2), 69.2 (OCH_2), 43.9 (cage CH), 32.6 (ArCH_2Ar), 31.5 (ArCH_2Ar), 30.2 (CH_2), 24.4 (CH_2), 23.8 (CH_2), 23.6 (CH_2), 11.3 (CH_3), 11.0 ppm (CH_3). MS (80 eV, ESI): *m/z* (%) = 1001.6 $[M]^-$ (calcd. 1001.6), 1024.6 [M + Na], 500.8 (100) $[M]^{2-}$ (calcd. 500.9).

Sodium Salts of 11a and 11b: A solution of resorc[4]arene cavitand **D** (0.105 g, 0.119 mmol) in THF (30 mL) was stirred for 30 min. Then solid NaH was tipped into the flask (0.02 g, 0.83 mmol) and stirring was continued for another 2 h and then the reaction mixture was heated at 65 °C for 2 h. A solution of **2** (0.142 g, 0.261 mmol) in THF (10 mL) was added dropwise over 1 h. The course of the reaction was monitored by TLC until the spot corresponding to **2** ($R_f \approx 0.25$, CH_3CN/CH_2Cl_2, 1:3) disappeared (30 h). After the reaction mixture had cooled to room temperature, it was carefully quenched by addition of ethanol (3 mL) followed by water (20 mL) and neutralized with acetic acid (4 M, a few drops) to pH 7. The resulting solution was evaporated under reduced pressure and water (20 mL) was added to the residue, whereupon the crude product was extracted with three portions of diethyl ether (3 × 20 mL). Water (5 mL) was added to the combined organic extracts and the solvents were evaporated to dryness. The residue was dried in vacuo. Twofold column chromatography (silica gel; column 1.5 × 25 cm) using CH_3CN/CH_2Cl_2 solvent mixtures (1:3 to 1:1) gave a yellow-orange band corresponding to compound **11** (mixture of both isomers **11a** and **11b**). Evaporation of the solvents gave the disodium salt of **11** as an orange powder; yield 110 mg (42%). The separation of the positional isomers was accomplished by medium pressure chromatography using a Merck LoBar® Lichroprep 60 system [column size B, elution with CH_3CN/CH_2Cl_2 (1:4); flow rate: 7 mL min^{-1}; UV detection: 312 nm]. The ascending part of the first peak was collected along with the descending part of the second overlapping peak.

$Na_2$11a (1,3-isomer): R_f = 0.33 (CH_3CN/CH_2Cl_2 1: 3); m.p. 162–165 °C. ^{1}H NMR (400 MHz, [D$_6$]acetone, 25 °C, TMS): δ = 7.9 (s, OH), 7.31 (s, 2 H, ArH), 7.04 (s, 2 H, ArH), 5.75–6.00 (m, 4 H, $ArOCH_2OAr$), 4.70 (t, $^3J_{H,H}$ = 8 Hz, 4 H, ArCHRAr), 4.38 (d, $^2J_{H,H}$ = 7 Hz, 4 H, $ArOCH_2OAr$), 3.93 (s, 8 H, cage CH), 3.50–3.75 (m, 8 H, OCH_2CH_2O), 3.37–3.50 (m, 8 H, OCH_2CH_2O), 2.20–2.45 (m, 8 H, CH_2CH), 1.73 (m, 24 H, CH_2), 0.92 ppm (t, $^3J_{H,H}$ = 6.8 Hz, 12 H, CH_3); B-H signals from ^{1}H{^{11}B-*selective*} NMR (400 MHz, [D$_6$]acetone, 25 °C, TMS): δ = 2.94 (H10′), 2.88 (H8′), 2.74 (H4′,7′), 2.42 (H10), 2.91, 1.81 (H4,7,9,9′,12,12′), 1.76 (H5′,11′), 1.65 (H5,11), 1.56 (H6′), 1.4 ppm (H6). ^{11}B NMR (128 MHz, [D$_6$]acetone, 25 °C, BF_3·Et_2O): δ = 23.3 (s, 2 B, B8), 4.4 (d, $^1J_{B,H}$ = 142 Hz, 2 B, B8′), 0.4 (d, $^1J_{B,H}$ = 139 Hz, 2 B, B10′), –2.4 (d, $^1J_{B,H}$ = 142 Hz, 2 B, B10), –4.5 (d, $^1J_{B,H}$ = 153 Hz, 4 B, B4′,7′), –7.3 (d, $^1J_{B,H}$ = 139 Hz, 8 B, B9,9′,12,12′), –7.9 (d, $^1J_{B,H}$ = 139 Hz, 4 B, B4,7), –17.3 (d, $^1J_{B,H}$ = 146 Hz, 4 B, B5′,11′), –20.5 (d, $^1J_{B,H}$ = 153 Hz, 4 B, B5,11), –22.0 (d, $^1J_{B,H}$ = 173 Hz, 2 B, B6′), –28.4 ppm (d, $^1J_{B,H}$ = 139 Hz, 2 B, B6). ^{13}C{^{1}H} NMR (101 MHz, [D$_6$]acetone, 25 °C, TMS): δ = 149.2, 149.0, 148.9, 145.4, 143.6, 140.1, 116.5 (ArC), 100.7 ($ArOCH_2OAr$), 73.8 (CH_2O), 72.5 (CH_2O), 71.7 (CH_2O), 69.2 (CH_2O), 54.5 (cage CH), 47.4 (cage CH), 38.1 (ArCHRAr), 29.3 (CH_2), 28.5 (CH_2), 26.1 (CH_2), 23.4 (CH_2), 14.5 ppm (CH_3). MS (54 eV, ESI): *m/z* = 853.3 (100) $[M]^{2-}$ (calcd. 853.5).

$Na_2$11b (1,2-isomer): R_f = 0.28 (CH_3CN/CH_2Cl_2, 1:3); m.p. 296–298 °C. ^{1}H NMR (400 MHz, [D$_6$]acetone, 25 °C, TMS): δ = 7.87 (s, 1 H, OH), 7.30 (s, 2 H, ArH), 7.04 (s, 2 H, ArH), 5.82–5.90 (m, 4 H, $ArOCH_2OAr$), 4.74 (m, 4 H, ArCHRAr), 4.37 (q, $^2J_{H,H}$ = 8 Hz, 4 H, $ArOCH_2OAr$), 4.38 (s, 8 H, cage CH), 3.54–3.65 (m, 8 H, OCH_2CH_2O), 3.41–3.48 (m, 8 H, OCH_2CH_2O), 2.30–2.35 (m, 8 H, CH_2CH), 1.31–1.40 (m, 24 H, CH_2), 0.93 ppm (t, $^3J_{H,H}$ = 7 Hz, 12 H, CH_3); B-H signals from ^{1}H{^{11}B-*selective*} NMR (400 MHz, [D$_6$]acetone, 25 °C, TMS): δ = 2.94 (H10′), 2.76 [H(4′,7′), 2.69 (H10), 2.53 (H8′), 2.06, 1.77 (H9,9′,12,12′), 1.74 (H4,7), 1.7 (H5′,11′), 1.66 (H5,11), 1.56 (H6′), 1.27 ppm (H6). ^{11}B NMR (128 MHz, [D$_6$]acetone, 25 °C, BF_3·Et_2O): δ = 23.2 (s, 2 B, B8), 4.3 (d, $^1J_{B,H}$ = 142 Hz, 2 B, B8′), 0.4 (d, $^1J_{B,H}$ = 139 Hz, 2 B, B10′), –2.4 (d, $^1J_{B,H}$ = 142 Hz, 2 B, B10), –4.4 (d, $^1J_{B,H}$ = 153 Hz, 4 B, B4′,7′), –7.3 (d, $^1J_{B,H}$ = 139 Hz, 8 B, B9,9′,12,12′), –8.0 (d, $^1J_{B,H}$ = 139 Hz, 4 B, B4,7), –17.3 (d, $^1J_{B,H}$ = 146 Hz, 4 B, B5′,11′), –20.5 (d, $^1J_{B,H}$ = 153 Hz, 4 B, B5,11), –21.9 (d, $^1J_{B,H}$ = 173 Hz, 2 B, B6′), –28.6 ppm (d, $^1J_{B,H}$ = 139 Hz, 2 B, B6); ^{13}C{^{1}H} NMR (101 MHz, [D$_6$]acetone, 25 °C, TMS): δ = 155.8, 149.0, 145.2, 143.2, 140.2, 133.2, 116.6 (ArC), 100.7 ($ArOCH_2OAr$), 74.3 (CH_2O), 73.8 (CH_2O), 71.1 (CH_2O), 69.1 (CH_2O), 54.4 (cage CH), 47.4 (cage CH), 39.95 (ArCHRAr), 32.7 (CH_2), 29.3 (CH_2), 28.5 (CH_2), 27.0 (CH_2), 23.4 (CH_2), 14.5 ppm (CH_3). MS (54 eV, ESI): *m/z* (%) = 853.4 (100) $[M]^{2-}$ (calcd. 853.5).

Sodium Salts of 12 and 13: A slurry of tetrakis(hydroxymethyl)resorc[4]arene cavitand **E** (75 mg, 0.080 mmol) in THF (30 mL) was stirred for 30 min. Then, NaH (5 mg, 0.21 mmol) was added and the reaction mixture was heated at 65 °C for 2 h. A solution of **2** (131 mg, 0.243 mmol) in THF (10 mL) was added dropwise over 1.5 h. The reaction was stopped, when the spot of **2** in the TLC had disappeared (20 h). After the reaction mixture had cooled to room temperature, the reaction was quenched by addition of ethanol (2 mL) followed by water (20 mL) and neutralized with a few drops of acetic acid (4 M). The resulting turbid solution was evaporated under reduced pressure almost to dryness, whereupon water was added (20 mL). The crude product was extracted with diethyl ether (3 × 20 mL). Water (5 mL) was added to the combined organic extracts and the solvents were evaporated to dryness. The residue was dried in vacuo, followed by separation by column chromatography (silica gel; column 1.5 × 20 cm) using $CHCl_3$/CH_3CN as the mobile phase, changing gradually its composition from pure $CHCl_3$ to 50% CH_3CN to give isolable products **12** and **13** after repeated chromatography. Disubstituted Na_2**12** and tetrasubstituted Na_4**13** compounds were obtained as orange solids.

$Na_2$12: Yield: 39 mg (27%); R_f = 0.22 (CH_3CN/CH_2Cl_2, 1:3); m.p. 296–298 °C. ^{1}H NMR (400 MHz, [D$_6$]acetone, 25 °C, TMS): δ = 8.01 (s, 2 H, ArH), 7.71 (s, 2 H, ArH), 5.98 (d, $^2J_{H,H}$ = 6 Hz, 4 H, $ArOCH_2OAr$), 4.96–5.02 (m, 4 H, ArCHRAr), 4.44 (s, 8 H, ArCH_2O), 4.37 (d, $^2J_{H,H}$ = 6 Hz, 8 H, $ArOCH_2OAr$), 4.24 (s, 8 H, cage CH), 3.60–3.65 (m, 8 H, OCH_2CH_2O), 3.51–3.56 (m, 8 H, OCH_2CH_2O), 1.99–2.05 (m, 8 H, CH_2CH), 1.79–1.82 (m, 24 H, CH_2), 1.25–1.31 ppm (m, 12 H, CH_3); B-H signals from ^{1}H{^{11}B-*selective*} NMR (400 MHz, [D$_6$]acetone, 25 °C, TMS): δ = 2.96 (H8′), 2.75 (H4′,7′), 2.71 (H10), 2.7 (H10′), 2.02, 1.81 (H9,9′,12,12′), 1.81 (H4,7), 1.8 (H5′,11′), 1.67 (H5,11), 1.55 (H6′), 1.48 (H6). ^{11}B NMR (128 MHz, [D$_6$]acetone, 25 °C, BF_3·Et_2O): δ = 23.2 (s, 2 B, B8), 4.5 (d, $^1J_{B,H}$ = 142 Hz, 2 B, B8′), 0.5 (d, $^1J_{B,H}$ = 139 Hz, 2 B, B10′), –2.5 (d, $^1J_{B,H}$ = 142 Hz, 2 B, B10), –4.4 (d, $^1J_{B,H}$ = 153 Hz, 4 B, B4′,7′), –7.3 (d, $^1J_{B,H}$ = 139 Hz, 8 B, B9,9′,12,12′), –7.8 (d, $^1J_{B,H}$ = 142 Hz, 4 B, B4,7), –17.3 (d, $^1J_{B,H}$ = 146 Hz, 4 B, B5′,11′), –20.4 (d, $^1J_{B,H}$ = 153 Hz, 4 B, B5,11), –22.1 (d, $^1J_{B,H}$ = 173 Hz, 2 B, B6′), –28.6 ppm (d, $^1J_{B,H}$ = 139 Hz, 2 B, B6). ^{13}C{^{1}H} NMR (101 MHz, [D$_6$]acetone, 25 °C, TMS): δ = 154.5, 139.9, 132.0, 129.6, 125.4, 121.9 (ArC), 100.9 ($ArOCH_2OAr$), 72.5 (CH_2-O), 70.6 (CH_2-O), 69.1 (CH_2-O), 68.7 (CH_2-

O), 63.7 (OCH_2-Ar), 55.0 (cage CH), 47.4 (cage CH), 40.1 (OCH_2-Ar), 33.4 (ArCHRAr), 32.2 (ArCHRAr), 29.6 (CH_2), 24.5 (CH_2), 23.3 (CH_2), 22.9 (CH_2), 14.3 ppm (CH_3).

$Na_4$13: Yield: 9 mg (5%); R_f = 0.06 (CH_3CN/CH_2Cl_2, 1:3); m.p. 159–160 °C. ^{1}H NMR (400 MHz, [D$_6$]acetone, 25 °C, TMS): δ = 7.72 (s, 4 H, ArH), 5.97 (d, $^2J_{H,H}$ = 7 Hz, 4 H, $ArOCH_2OAr$), 4.98 (q, $^3J_{H,H}$ = 8 Hz, 4 H, ArCHRAr), 4.44 (s, 8 H, $ArCH_2O$), 4.37 (d, $^2J_{H,H}$ = 7 Hz, 4 H, $ArOCH_2OAr$), 4.25 (s, 16 H, cage CH), 3.63-3.69 (m, 16 H, 2 OCH_2CH_2O), 3.60–3.52 (m, 16 H, OCH_2CH_2O), 2.05–2.11 (m, 8 H, CH_2CH), 1.80–1.93 (m, 24 H, CH_2), 1.23–1.29 ppm (m, 12 H, CH_3); B-H signals from ^{1}H{^{11}B-*selective*} NMR (400 MHz, [D$_6$]acetone, 25 °C, TMS): δ = 2.96 (H8′), 2.78 (H4′,7′), 2.75 (H10), 2.55 (H10′), 2.01 1.8 (H9,9′,12,12′), 1.81 (H4,7), 1.79 (H5′,11′), 1.68 (H5,11), 1.58 (H6′), 1.26 ppm (H6). ^{11}B NMR (128 MHz, [D$_6$]acetone, 25 °C, BF_3·Et_2O): δ = 23.2 (s, 4 B, B8), 4.3 (d, $^1J_{B,H}$ = 142 Hz, 4 B, B8′), 0.5 (d, $^1J_{B,H}$ = 139 Hz, 4 B, B10′), –2.5 (d, $^1J_{B,H}$ = 142 Hz, 4 B, B10), –4.4 (d, $^1J_{B,H}$ = 153 Hz, 8 B, B4′,7′), –7.4 (d, $^1J_{B,H}$ = 139 Hz, 16B, B9,9′,12,12′), –8.1 (d, $^1J_{B,H}$ = 142 Hz, 8 B, B4,7), –17.3 (d, $^1J_{B,H}$ = 146 Hz, 8 B, B5′,11′), –20.4 (d, $^1J_{B,H}$ = 153 Hz, 8 B, B5,11), –22.1 (d, $^1J_{B,H}$ = 173 Hz, 4 B, B6′), –28.5 ppm (d, $^1J_{B,H}$ = 139 Hz, 4 B, B6). ^{13}C{^{1}H} NMR (101 MHz, [D$_6$]acetone, 25 °C, TMS): δ = 154.4, 139.9, 125.4, 122.0 (ArC), 100.9 ($ArOCH_2OAr$), 72.5 (CH_2O), 70.8 (CH_2O), 70.7 (CH_2O), 69.1 (CH_2O), 63.7 (CH_2Ph), 54.8 (cage CH), 47.4 (cage CH), 32.2 (ArCHRAr), 29.2 (CH_2), 28.9 (CH_2), 21.5 (CH_2), 16.4 ppm (CH_3).

Sodium Salt of 14: A slurry of resorc[4]arene cavitand **F** (105 mg, 0.127 mmol) in THF (15 mL) was stirred for 30 min. Then, solid NaH (5 mg, 0.21 mmol) was added, and the reaction mixture was stirred at 45 °C for 2 h. A solution of **2** (138 mg, 0.255 mmol) in THF (5 mL) was added dropwise from a syringe through a septum over 1 h. The reaction was stopped when the spot of **2** in the TLC had disappeared (30 h). The reaction mixture was cooled to room temperature, and the reaction was quenched by careful addition of ethanol (1 mL), water (10 mL), and neutralized with a few drops of hydrochloric acid (0.25 N). THF was removed under reduced pressure, and the residue was filtered and dried in vacuo. Purification was performed by repeated column chromatography (silica gel; column 1.5×20 cm) using CH_3CN/CH_2Cl_2 mixtures as mobile phase, gradually increasing the content of CH_3CN from 10% to 40%. The main orange band was collected to give, after evaporation of the solvent, Na_2**14** as an orange powder; yield 67 mg (31%). Part of the product was transformed into the dicaesium salt. Thus, a solution of Na_2**14** (30 mg) in diethyl ether (3 mL) was treated three times with diluted HCl (3 M, 3 mL). The organic layer was separated and, after addition of H_2O (0.5 mL), the solution was evaporated to dryness. The residue was dissolved in 50% aqueous EtOH (ca. 20 mL), after which an aqueous solution of CsCl (20 mg in 1 mL of H_2O) was added. After evaporation of the solvents the resulting solid was washed with 20% aqueous EtOH (10 mL). The filtrate was concentrated and 50% ethanol (15 mL) was added to the residue. The resulting suspension was heated at 80 °C and EtOH (96%) was then added dropwise until complete dissolution. Upon cooling, the orange solid was collected by filtration to give Cs_2**14** (33 mg).

$Na_2$14: R_f = 0.28 (CH_3CN/CH_2Cl_2, 1:3); m.p. 242–245 °C.

$Cs_2$14: ^{1}H NMR (400 MHz, [D$_6$]acetone, 25 °C, TMS): δ = 7.51 (s, 2 H, ArH), 7.48 (s, 2 H, ArH), 5.91–5.93 (2d, 4 H, $ArOCH_2OAr$), 4.78–4.82 (m, 4 H, ArCHRAr), 4.29 (d, $^2J_{H,H}$ = 7 Hz, 4 H, $ArOCH_2OAr$), 4.19 (s, 8 H, cage CH), 3.61–3.66 (m, 16 H, OCH_2CH_2O), 3.53–3.60 (m, 8 H, CH_2O), 2.91 (s, 6 H, CH_3Ar), 2.57 (s, 6 H, CH_3Ar), 2.39–2.41 (m, 8 H, CH_2), 1.57–1.62 ppm (m, 8 H, CH_2); B-H signals from ^{1}H{^{11}B-*selective*} NMR (400 MHz, [D$_6$]acetone, 25 °C, TMS): δ = 2.95 (H10′), 2.85 (H8′), 2.76 (H4′,7′), 2.7 (H10), 2.1, 1.81 (H9,9′,12,12′), 2.01 (H4,7), 1.66 (H5′,11′), 1.56 (H5,11), 1.55 (H6′), 1.96 ppm (H6). ^{11}B NMR (128 MHz, [D$_6$]acetone, 25 °C, BF_3·Et_2O): δ = 23.2 (s, 2 B, B8), 4.5 (d, $^1J_{B,H}$ = 142 Hz, 2 B, B8′), 0.5 (d, $^1J_{B,H}$ = 155 Hz, 2 B, B10′), –2.5 (d, $^1J_{B,H}$ = 142 Hz, 2 B, B10), –4.4 (d, $^1J_{B,H}$ = 153 Hz, 4 B, B4′,7′), –7.3 (d, $^1J_{B,H}$ = 139 Hz, 8 B, B9,9′,12,12′), –7.9 (d, $^1J_{B,H}$ = 142 Hz, 4 B, B4,7), –17.2 (d, $^1J_{B,H}$ = 146 Hz, 4 B, B5′,11′), –20.4 (d, $^1J_{B,H}$ = 153 Hz, 4 B, B5,11), –22.0 (d, $^1J_{B,H}$ = 173 Hz, 2 B, B6′), –28.4 ppm (d, $^1J_{B,H}$ = 165 Hz, 2 B, B6). ^{13}C{^{1}H} NMR (101 MHz, [D$_6$]acetone, 25 °C, TMS): δ = 154.1, 139.0, 138.2, 124.8, 124.7, 119.8, 119.7 (ArC), 99.4 ($ArOCH_2OAr$), 72.6 (CH_2O), 71.7 (CH_2O), 70.9 (CH_2O), 70.7, 69.2, 62.3 (CH_2-O), 54.7 (cage CH), 47.4 (cage CH), 37.9 (ArCHRAr), 37.7 (ArCHRAr), 32.1 (CH_3Ar), 28.9 (CH_2), 28.7 (CH_2), 26.9 ppm (CH_2). MS (70 eV, ESI): *m*/*z* (%) = 824.6 (100) $[M + Na - H]^{2-}$, (calcd. 824.5), 1674.8 (14) [M + Na + H] (calcd. 1674.9).

Sodium Salt of 15: The synthesis was carried out as described for compound **14**, but the ratio of reagents was 1:4; resorc[4]arene cavitand **F** (192 mg, 0.233 mmol) was treated with NaH (27 mg, 1.12 mmol) and **2** (505 mg, 0.931 mmol) in THF (20 mL). During final chromatographic purification, elution was accomplished by increasing the CH_3CN content from 10% to 50%. The main orange band was collected corresponding to an R_f value of 0.11 in the TLC (CH_3CN/CH_2Cl_2, 1:3). Yield of sodium salt Na_4**14**: 192 mg (32%).

$Na_4$15: R_f = 0.11 (CH_3CN/CH_2Cl_2, 1:3), m.p. 212–214 °C. ^{1}H NMR (400 MHz, [D$_6$]acetone, 25 °C, TMS): δ = 7.48 (s, 4 H, ArH), 5.92 (d, $^2J_{H,H}$ = 7 Hz, 4 H, $ArOCH_2OAr$), 4.81 (t, $^3J_{H,H}$ = 7 Hz, 4 H, ArCHRAr), 4.30 (d, $^2J_{H,H}$ = 7 Hz, 4 H, $ArOCH_2OAr$), 4.23 (s, 8 H, cage CH), 3.59–3.66 (m, 16 H, OCH_2CH_2O), 3.52–3.57 (m, 16 H, OCH_2CH_2O), 3.38–342 (m, 8 H, CH_2O), 2.85 and 2.88 (s, 6 H, CH_3O), 2.38–2.56 (m, 8 H, CH_2), 1.61–1.65 ppm (m, 8 H, CH_2); B-H signals from ^{1}H{^{11}B-*selective*} NMR (400 MHz, [D$_6$]acetone, 25 °C, TMS): δ = 2.98 (H10′), 2.85 (H8′), 2.75 (H4′,7′), 2.7 (H10), 2.06, 1.81 (H9,9′,12,12′), 2.01 (H4,7), 1.66 (H5′,11′), 1.55 (H5,11), 1.55 (H6′), 1.45 ppm (H6). ^{11}B NMR (128 MHz, [D$_6$]acetone, 25 °C, BF_3·Et_2O): δ = 23.28 (s, 4 B, B8), 4.3 (d, $^1J_{B,H}$ = 149 Hz, 4 B, B8′), 0.5 (d, $^1J_{B,H}$ = 155 Hz, 4 B, B10′), –2.4 (d, $^1J_{B,H}$ = 142 Hz, 4 B, B10), –4.4 (d, $^1J_{B,H}$ = 164 Hz, 8 B, B4′,7′), –7.3 (d, $^1J_{B,H}$ = 138 Hz, 16B; B9,9′,12,12′), –7.9 (d, $^1J_{B,H}$ = 142 Hz, 8 B, B4, 7), –17.3 (d, $^1J_{B,H}$ = 164 Hz, 8 B, B5′,11′), –20.4 (d, $^1J_{B,H}$ = 171 Hz, 8 B, B5,11), –22.0 (d, $^1J_{B,H}$ = 173 Hz, 4 B, B6′), –28.4 ppm (d, $^1J_{B,H}$ = 165 Hz, 4 B, B6). ^{13}C{^{1}H} NMR (101 MHz, [D$_6$]acetone, 25 °C, TMS): δ = 154.2, 138.8, 135.3, 119.8 (ArC), 99.4 ($ArOCH_2OAr$), 72.6 (CH_2O), 71.0 (CH_2O), 70.7 (CH_2O), 69.2 (CH_2O), 55.1 (cage CH), 47.4 (cage CH), 37.7 (ArCHRAr), 30.4 (CH_3Ar), 27.4 (CH_2), 27.2 ppm (CH_2). MS (70 eV, ESI): *m*/*z* (%) = 618.65 $[M - H]^{4-}$ (100) (calcd. 618.9), 832.9 (25) $[M + Na]^{3-}$ (calcd. 833.3).

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