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Decorating Poly(alkyl aryl-ether) Dendrimers with Metallacarboranes

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A new family of polyanionic poly(alkyl aryl-ether) metallodendrimers decorated with four and eight cobaltabisdicarbollide units have been obtained in high yield by the ring-opening reaction of cyclic oxonium [3,3′-Co(8-$(C_2H_4O)_2$-1,2-$C_2B_9H_{10}$)-(1′,2′-$C_2B_9H_{11}$)] with alkoxides formed by deprotonation of terminal alcohols in the α,α′-bis[3,5-bis(hydroxymehyl)phenoxy]-*p*-xylene, α,α′-bis[3,5-bis(hydroxymehyl)phenoxy]-*m*-xylene, α,α′-bis[3,5-bis-[3,5-bis(hydroxymethyl)phenoxy]methylen]-phenoxy]-*p*-xylene, and α,α,′-bis[3,5-bis-[3,5-bis(hydroxymethyl)phenoxy]methylen]phenoxy]-*m*-xylene dendrimers. The crystal structure of the precursor α,α′-bis[3,5-bis(chloromethyl)phenoxy]-*p*-xylene is also described. Final products are fully characterized by FTIR, NMR, UV−vis spectroscopies and elemental analysis. For metallodendrimers, the UV−vis absorptions have been a good tool for estimating the experimental number of cobaltabisdicarbollide units peripherally attached to the dendrimeric structure and consequently to corroborate the complete functionalization of the dendrimers.

Introduction

Cobaltabisdicarbollide, $[(3,3'\text{-Co-}(1,2\text{-}C_2B_9H_{11})_2]^-$,[1] is a boron-rich monoanionic cluster, that has extraordinary chemical and thermal stability, lipophilicity,[2] weakly coordinating character,[3] and low nucleophilicity. There are two main ways to functionalize a cobaltabisdicarbollide anion, by linking functional groups on the cluster carbon atoms[4] or on the cluster boron atoms.[4b,5] Substitution at boron has been achieved under Friedel−Crafts conditions,[6] Kumada type reactions,[5] or with strong alkylating agents.[5a,7] Nevertheless, after the synthesis of the zwitterionic compound [3,3′-Co(8-$(C_2H_4O)_2$-1,2-$C_2B_9H_{10}$)(1′,2′-$C_2B_9H_{11}$)] a great advance on the synthesis of polyanionic macromolecules incorporating cobaltabisdicarbollide was achieved.[4b,8] This compound has been shown to be susceptible to nucleophilic attack on the positively charged oxygen atom resulting in an anionic species formed by the opening of the dioxane ring.[9] The latter was

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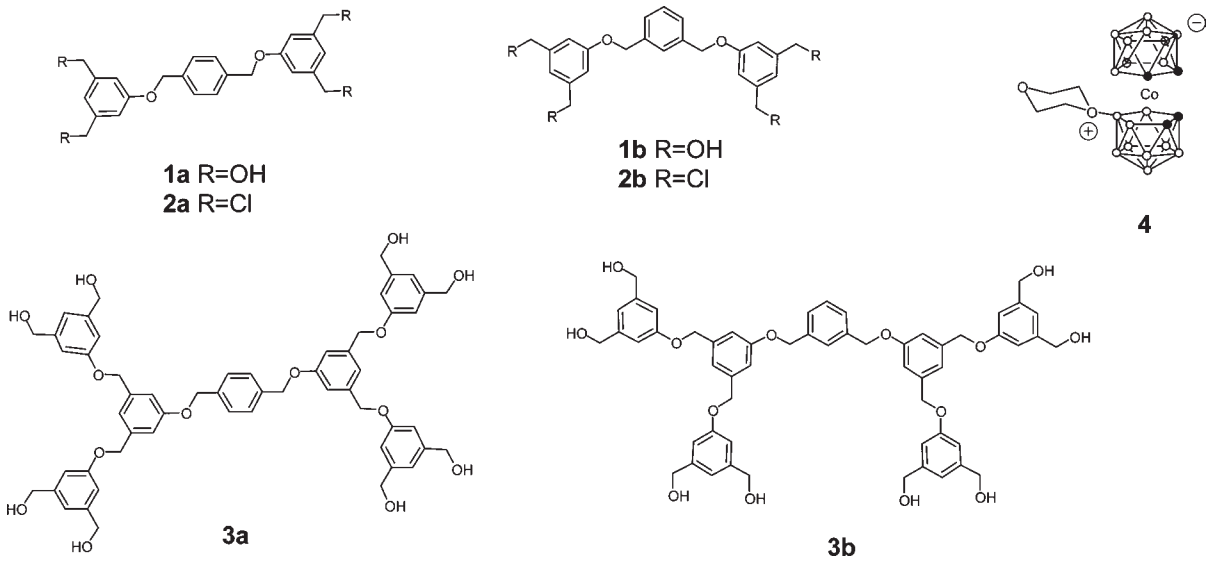
Chart 1. Starting Poly(alkyl aryl-ether) Dendrimers and Cobaltabisdicarbollide Derivative



covalently bonded to the periphery of scaffolds such as nucleosides,[10] porphyrins,[11] and calixarens,[9c,12] among others.[9d] The $[(3,3'\text{-Co-}(1,2\text{-}C_2B_9H_{11})_2]^-$ is suitable for a wide range of applications, such as the extraction of radionuclides,[9c,13] doping agent in conducting polymers,[2c,14] in ion selective PVC membrane electrodes for medical drug analysis,[15] as boron rich carriers for cancer treatment and diagnosis in Boron Neutron Capture Therapy (BNCT),[16] among others.[17] The $[(3,3'\text{-Co-}(1,2\text{-}C_2B_9H_{11})_2]^-$ can be delivered into tumor cells using different strategies for tumor targeting or can be used as building blocks for the synthesis of boron-containing biomolecules. Following our interest in developing water-soluble boron-rich anionic dendrimeric systems,[18] we have recently reported the use of an appropriate derivative of the monoanionic cobaltabisdicarbollide, $Cs[1,1'\text{-}\mu\text{-SiMeH-}3,3'\text{-Co}(1,2\text{-}C_2B_9H_{10})_2]$,[4c,d] to be peripherally attached to dendrimers of different nature.[19] In that case, the strategy was based on the regiospecific hydrosylilation reactions on terminal alkene functions with $[1,1'\text{-}\mu\text{-SiMeH-}3,3'\text{-Co}(1,2\text{-}C_2B_9H_{10})_2]^-$ under the presence of Karstedt catalyst, and subsequently cobaltabisdicarbollide units were bonded through the carbon atoms to the dendrimers. In this work, we have attached units through the boron atom in position 8, taking into account the successful reaction of the dioxane-metallacarborane derivative, $[3,3'\text{-Co}(8\text{-}C_4H_8O_2\text{-}1,2\text{-}C_2B_9H_{10})(1',2'\text{-}C_2B_9H_{11})]$ with nucleophiles.[8] For that purpose we have chosen Fréchet-type poly(alkyl aryl-ether) dendrimers[20] as platforms because of their biocompatible properties and biomedical applications,[21] such as drug delivery.[21d]

Results and Discussion

Synthesis and Characterization of Starting Alcohol-Terminated Poly(Alkyl Aryl-Ether) Compounds. The tetrahydroxybenzyl **1a** and **1b** and tetrachlorobenzyl derivatives **2a** and **2b**[22] (see Chart 1) were prepared as described previously.[23]

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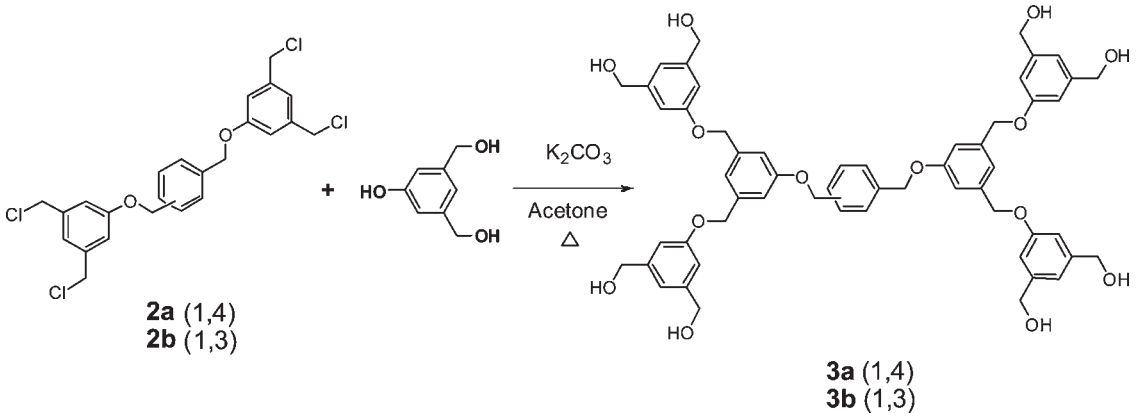
Scheme 1. Preparation of Compounds **3a** and **3b**



The octahydroxybenzyl derivatives **3a** and **3b** were prepared in 78% and 77% yield, respectively, by reaction of α,α′-bis-[3,5-bis(chloromethyl)phenoxy]-*p*-xylene (**2a**) and α,α′-bis-[3,5-bis(chloromethyl)phenoxy]-*m*-xylene (**2b**) with 4 equiv of 3,5-bishydroxymethylphenol, in the presence of K_2CO_3 at reflux of acetone for 96 h (Scheme 1).

Evidence for the formation of the alcohols **3a** and **3b** was obtained from ^{1}H and $^{13}C\{^1H\}$ NMR, IR, and mass spectrometry (MS). As an example, the ^{1}H NMR spectrum of **3a** shows methylene signals at 5.12 and 5.05 ppm that integrate for 8 protons, as well as a broad singlet at 4.45 ppm integrating for 16 protons that correspond to benzylic methylenes. Resonances between 7.07 and 6.83 ppm attributed to aromatic protons of the new bishydroxymethylphenoxy have also been observed. The $^{13}C\{^1H\}$ NMR spectrum of **3a** show new methylene resonances at 63.5 ppm. Both isomers, **3a** and **3b**, produced an MH^+ ion at m/z = 955 in the FAB mass spectra. The tetrachloro derivative **2a** crystallized by slow evaporation of a saturated solution of the methylene chloride during the course of the preparation of the alcohol-terminated poly(alkyl aryl-ether) compounds. The X-ray structure of **2a** (Figure 1) showed that the molecule is related by a crystallographic inversion center with half of the molecule in the asymmetric unit. The chloromethyl-phenoxy fragments attached to the C9/C9′ atoms are placed in opposite sides of the mean plane defined by the central aromatic ring. This conformation allows the establishment of constructive $\pi-\pi$ stacking interactions along the crystal packing of the molecules (Figure 2). Further details of data collection and structure refinement are given in Table 1 and the Supporting Information.

Peripheral Functionalization with Cobaltabisdicarbollide. To decorate the periphery of previously prepared compounds **1a**−**b** and **3a**−**b** with cobaltabisdicarbollide, the zwitterionic oxonium [3,3′-Co(8-$C_4H_8O_2$-1,2-$C_2B_9H_{10}$)-(1′,2′-$C_2B_9H_{11}$)] (**4**) was used (see Chart 1), taking advantage of the reactivity of **4** toward nucleophiles such as alkoxylates and phenolates to produce the ring-opening reaction.[4b,24] Thus the first step involved the deprotonation of the terminal alcohols **1a**−**b** and **3a**−**b** with K[*t*-BuO] in dimethyl sulfoxide (DMSO) to give the corresponding alkoxides, which were reacted in situ with

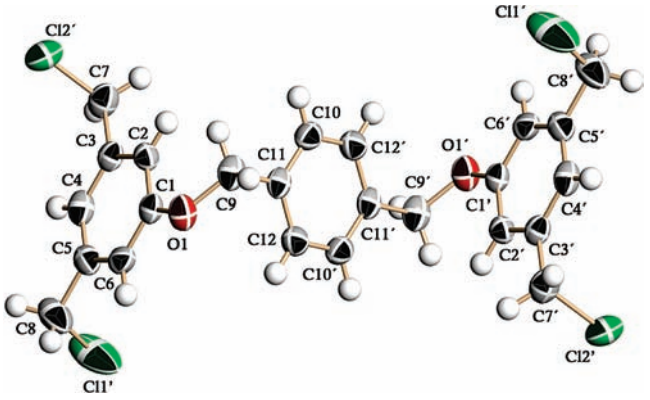


Figure 1. Molecular structure of **2a** showing the atom-numbering scheme. Displacements ellipsoids are drawn at the 50% probability level, and the H atoms are shown as spheres of arbitrary radii.

stoichiometric amounts of **4** to achieve the preparation of tetrafunctionalized dendrimers **5a** and **5b** in 51 and 62% yields, and the octafunctionalized dendrimers **6a** and **6b** in 41 and 47% yields, respectively (Scheme 2).

It is important to note that the difficulty in the synthesis of these compounds does not lie in the functionalization with the cobaltabisdicarbollide derivative **4**, but in the preparation of the nucleophiles. The reactions were performed in DMSO because the solubility of the starting alcohols **1a**−**b** and **3a**−**b** and their corresponding salts in aprotic solvents is extremely low, and compound **4** is only soluble in polar solvents. Therefore the only two available solvents for the reaction were dimethylformamide (DMF) and DMSO. It is mandatory that the only nucleophiles present in the reaction media be the dendrimeric alkoxides, so that care must be taken to exclude water, since the excess of base increases the concentration of OH^- anions leading to cleavage of the oxonium ring in **4** and preventing the reaction with the dendrimers. To improve the deprotonation reaction, K[*t*-BuO] was selected as the base, because of its easy manipulability and adequate pK_a to deprotonate the benzyl alcohols, allowing us to use it in stoichiometric amounts. Other bases used in previous works,[24,25] such as BuLi or NaH, gave poor yields because of their

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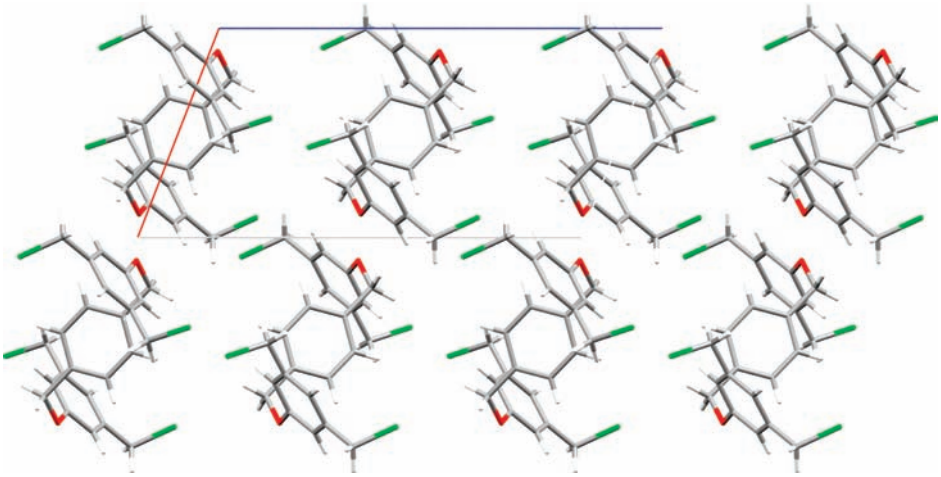


Figure 2. Crystal packing of compound **2a** showing $\pi-\pi$ stacking.

Table 1. Selected Crystal and Refinement Data for Compound **2a**

	2a
formula	$C_{24}H_{22}Cl_4O_2$
molecular weight (g/mol^{-1})	484.22
crystal system	monoclinic
space group	$P2_1/c$
a (Å)	8.3535(3)
b (Å)	8.9145(3)
c (Å)	16.5937(6)
α (deg)	90
β (deg)	111.359(2)
γ (deg)	90
V (Å^3)	1150.82(7)
Z	2
ρ_{calc} (g/cm^3)	1.397
collected reflections	6345
independent reflections (R_{int})	2538 (0.053)
observed reflections	1848
$R1[I > 2\sigma(I)]^a$	0.066
Rw (all data)^b	0.169
$\Delta\rho_{max}$ (e Å^{-3})	0.46
$\Delta\rho_{min}$ (e Å^{-3})	−0.56
GOOF	1.06

^{a} $R = \sum[w(F_o^2 - F_c^2)/\sum F_o^2$. ^{b} $R_w = \sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2$.

solubility problems in DMSO and low reactivity. The addition of the base was done at room temperature, and it was allowed to stand under stirring for 30 min. Afterward, cobaltabisdicarbollide **4** was added, and the resulting mixture was stirred 24 h. The reaction was monitored by thin layer chromatography (TLC) following the disappearance of the signal corresponding to compound **4**. Dendrimers **5a**, **5b**, **6a**, and **6b** (see Figure 3) were isolated as orange solids after evaporation of the solvent, and addition of a minimum volume of EtOH to the oily residue followed by a saturated aqueous solution of CsCl.

Characterization of Metallodendrimers. Metallodendrimers **5a**, **5b**, **6a**, and **6b** were characterized on the basis of FT-IR, ^{1}H, ^{11}B, ^{13}C{^{1}H} NMR (see spectra in the Supporting Information), and UV−vis spectroscopies, matrix-assisted laser desorption/ionization-time of flight mass spectrometry (MALDI-TOF-MS), elemental analyses, and high performance liquid chromatography (HPLC). All compounds present strong bands for *closo* clusters around 2550 cm^{-1} typical for υ(B−H) in the IR spectra, bands around 2952, 2920, and 2870 cm^{-1}, that correspond to $\upsilon(C_{alkyl}-H)$ and the band characteristic of $\upsilon(C_c-H)$ about 3040 cm^{-1}. The ^{1}H NMR spectra show resonances between 7.62 and 6.93 ppm attributed to the aromatic protons. The resonance centered at 4.45 ppm (4.60 ppm in acetone-d$_6$) attributed to the benzylic methylene bonded to the OH in the starting dendrimers appears as two close signals, whereas after functionalization it has changed to an only peak at 4.55 ppm. The C_c-H proton chemical shifts are indicative of the ring-opening, since they appear at higher frequencies (between 4.11 and 4.23 ppm) compared with the starting **4** (3.94 ppm). In addition other resonances between 3.55 and 3.65 ppm corresponding to $-OCH_2-$ protons also appeared. The ^{13}C{^{1}H} NMR spectra show different resonances in the aromatic region, from 160.5 to 100.5 ppm for all compounds. Depending on the metallodendrimer, different resonances attributed to the carbon atoms of the ether groups ($-OCH_2-$) are observed in the range 68.00 to 73.00 ppm. After functionalization with cobaltabisdicarbollide units, resonances around 53.00 and 46.0 ppm attributed to the C_c-*H* atoms are observed.

The ^{11}B{^{1}H} NMR spectra of metallodendrimers show an identical 1:1:1:1:2:2:4:2:2:1:1 pattern in the region from +25 to −28 ppm. The boron resonance with a relative intensity of 4 is due to a coincidental overlap of two resonances with a 2:2 relative intensity. This pattern indicates a C_s symmetry for the cobaltabisdicarbollide unit after ring-opening with only a symmetry plane, compared to the C_{2v} symmetry shown by the unsubstituted [3,3′-Co(1,2-$C_2B_9H_{11}$)$_2$]$^-$, that displays a 2:2:8:4:2 pattern. As expected, the resonance at lowest field in the ^{11}B{^{1}H} NMR spectra corresponds to the B(8) substituted boron atom (B−O) and remains as a singlet in the ^{11}B NMR. The mean $\langle\delta\rangle$ value of the ^{11}B NMR spectrum of each compound is around −6.6, that is, in the range observed for previously reported metallacarborane-containing aryl-ether derivatives (−6.3 and −6.8 ppm).[24]

The MALDI-TOF-MS spectra of metallodendrimers **5a**, **5b**, **6a**, and **6b** were recorded in the negative ion mode without matrix, where an extensive fragmentation had occurred. This fragmentation phenomenon was previously observed for cobaltabisdicarbollide-containing carbosilane and carbosiloxane dendrimers.[19] Thus, this technique

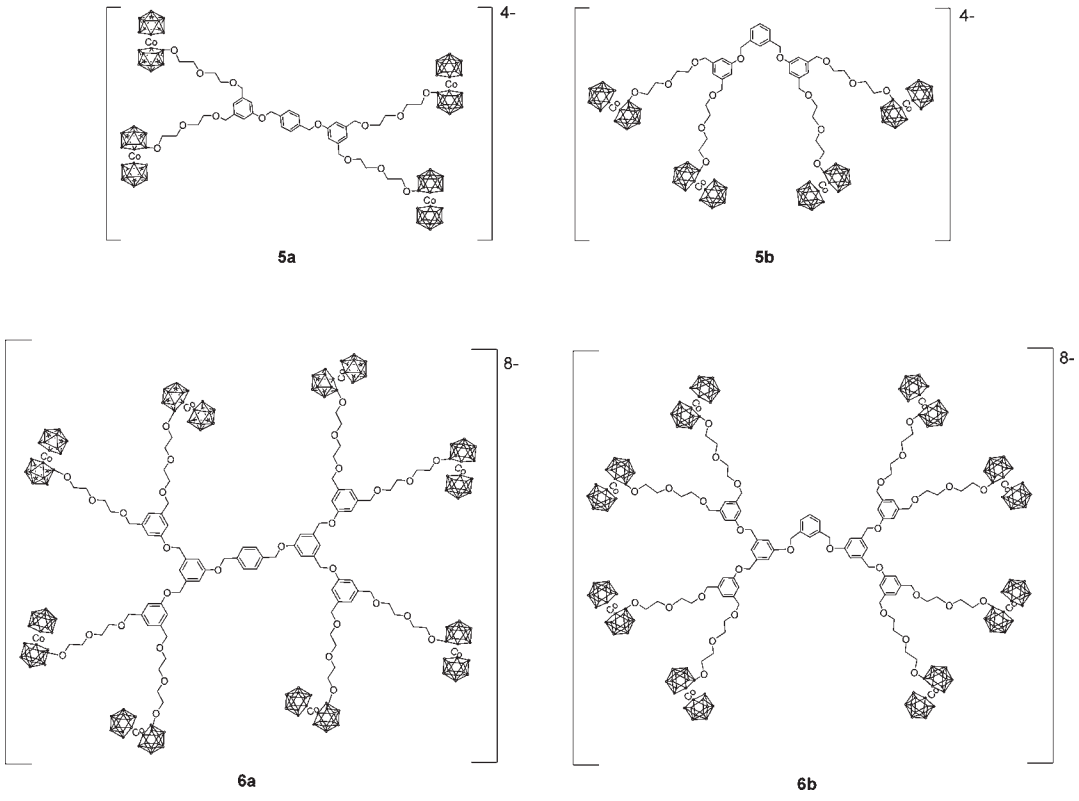
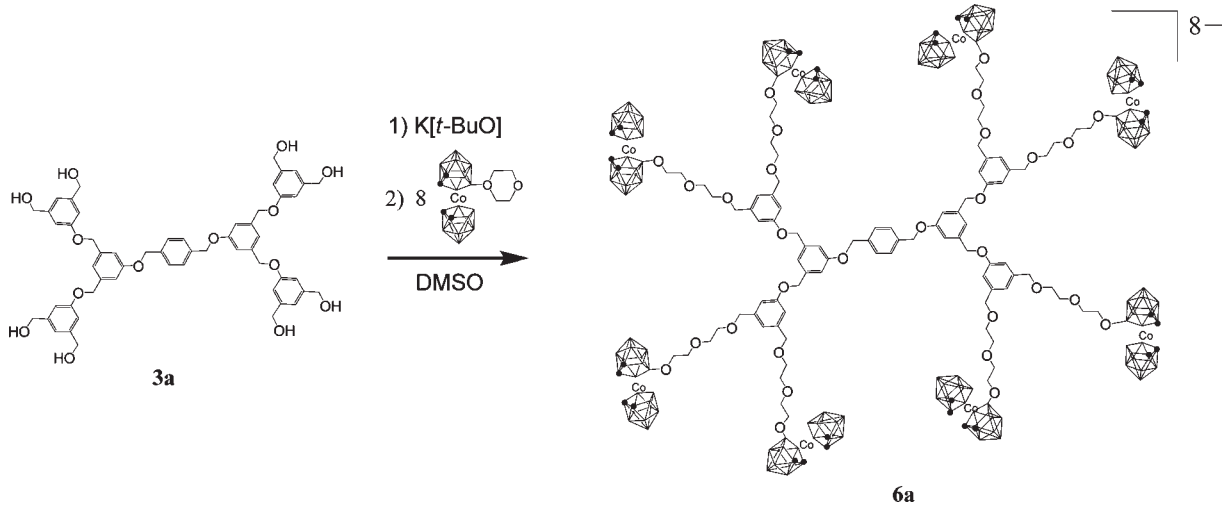


Figure 3. Molecular representation of the different cobaltabisdicarbollides-containing poly(alkyl aryl-ether) metallodendrimes, **5a**, **5b**, **6a**, and **6b**.

Scheme 2. Preparation of Cobaltabisdicarbollide-Containing Poly(alkyl aryl-ether) Metallodendrimer **6a**



cannot be used to fully characterize this type of boron-containing dendrimers.[26]

The UV−vis absorption measurements for compounds **5a**, **5b**, **6a**, and **6b** were performed in EtOH. Table 2 lists the spectroscopic data obtained for these compounds. Cobaltabisdicarbollide containing metallodendrimers show three absorption bands, the first one in the region 268−274 nm, a second band between 310 and 312 nm, and the third one between 369 and 372 nm (Figure 4), typical for compounds bearing cobaltabisdicarbollide units bonded through $-O-(CH_2)_2-O-(CH_2)_2-B(8)$.

As was already found for metallocene-containing dendrimers,[27] and in previously reported cobaltabisdicarbollide-containing dendrimers, the UV−vis spectroscopy has been a suitable method to estimate the number of metallocarborane units.[19] If the Beer−Lambert Law is followed, the molar absorptivities (ε_{max}) of the cobaltabisdicarbollide-containing dendrimers must be proportional to the number of metallacarboranes attached to the periphery. The number of cobaltabisdicarbollide fragments for each dendrimer can be estimated by comparing the absorptivity (ε) of the dendrimers with that obtained for the monomer

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Table 2. UV-vis Spectroscopic Data for Dendrimers **5a**, **5b**, **6a**, and **6b**

dendrimer	λ (ε)[a]		
5a	268 (69.7)	310 (110.9)	372 (16.4)
5b	273 (56.6)	312 (117.6)	371 (18.8)
6a	274 (99.4)	312 (217.0)	370 (35.8)
6b	273 (109.7)	311 (220.0)	369 (35.2)

[a] ε [10^{-3} dm^3 mol^{-1} cm^{-1}].

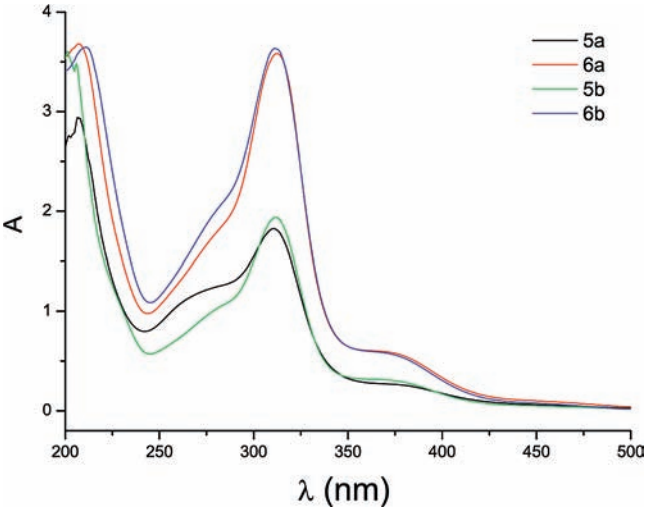

Figure 4. UV−vis spectra for metallacarborane-containing dendrimers **5a**, **5b**, **6a**, and **6b** in EtOH solutions at 1.6×10^{-5} M.

Table 3. Number of Cobaltabisdicarbollide Units Calculated for the Metallocarborane-Terminated Dendrimers Using the Beer−Lambert Law

compound	λ[nm]	theoretical no. of cobaltabisdicarbollides	ε	calculated no. of cobaltabisdicarbollides[a]
monomer	310	1	ε_0 = 28.3	
5a	310	4	110.9	3.9
5b	312	4	117.6	4.2
6a	312	8	217.0	7.7
6b	311	8	220.0	7.8

[a] $\varepsilon/\varepsilon_0$: represents the experimental cobaltabisdicarbollide number calculated from the Beer−Lambert Law.

[3,3′-Co(8-OCH$_2$CH$_2$−O−CH$_2$CH$_2$−OCH$_3$-1,2-C$_2$B$_9$H$_{10}$)-(1′,2′-C$_2$B$_9$H$_{11}$)]$^-$ (ε_0).[4b] Table 3 shows the molar absorptivity values (ε) for all metallodendrimers and the calculated number of cobaltabisdicarbollide units using the Beer−Lambert Law at λ = 310 nm. The number of metallacarboranes calculated fits well with the theoretical numbers, corroborating the complete functionalization of the different metallacarborane-containing dendrimers (Figura 5).

The chromatographic behavior of metallodendrimers **5a**, **5b**, **6a**, and **6b** was examined using a C18 reverse phase column with pure HPLC quality methanol as mobile phase. This chromatographic method could be optimized to obtain a larger difference in retention times between these compounds if instead of pure methanol the mobile phase is prepared by mixing methanol and water. However, the objective for this paper was to study the behavior of these metallodendrimers using reverse phase HPLC. Retention time measurements for methanol solutions of these metallodendrimers showed that **6a** and **6b** had a slightly lower retention time profiles than the smaller

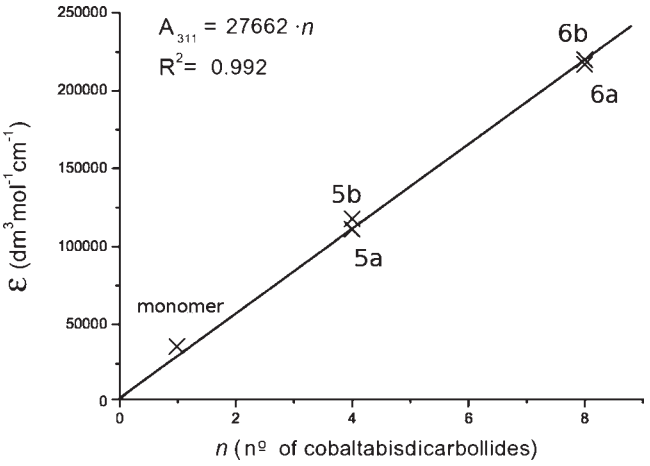

Figure 5. Linear correlation between the number of cobaltabisdicarbollide units attached to the periphery and the absorptivity at λ = 310 nm. Monomer: [3,3′-Co(8-OCH$_2$CH$_2$−O−CH$_2$CH$_2$−OCH$_3$-1,2-C$_2$B$_9$H$_{10}$)-(1′,2′-C$_2$B$_9$H$_{11}$)]$^-$

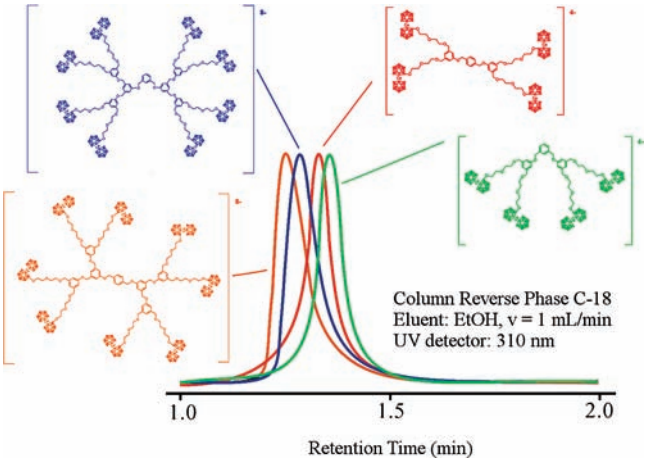

Figure 6. HPLC retention times obtained for metallodendrimers using a C18 reverse phase column and MeOH as mobile phase.

Table 4. HPLC Retention Time Obtained for Metalodendrimers **5a**, **5b**, **6a**, and **6b**

compound	retention time (min)
monomer	1.31
5a	1.38
5b	1.39
6a	1.32
6b	1.31

dendrimers **5a** and **5 b**, see Figure 6. The monomer [3,3′-Co(8-OCH$_2$CH$_2$−O−CH$_2$CH$_2$−OCH$_3$-1,2-C$_2$B$_9$H$_{10}$)(1′,2′-C$_2$B$_9$H$_{11}$)]$^-$ was chosen as a reference compound and showed the lowest retention time, although very close to the profiles reached by compounds **6a**−**b**, see Table 4. The difference between the retention times is not very significant. Nevertheless, values seem to suggest that, under these conditions, metallodendrimers with higher number of peripheral anionic cobaltabisdicarbollide units surrounding the aromatic dendrimeric structure induce strong hydrophilic character, that lowers its retention time in the hydrophobic column.

Conclusions

A new family of high boron-content polyanionic poly(alkyl aryl-ether) metallodendrimers decorated with four or

eight cobaltabisdicarbollide units has been successfully synthesized following the ring-opening reaction of zwitterion [3,3′-Co(8-(C_2H_4O)$_2$-1,2-$C_2B_9H_{10}$)(1′,2′-$C_2B_9H_{11}$)]. For that purpose, tetrahydroxybenzyl and octahydroxybenzyl poly(alkyl aryl-ether) dendrimers with four and eight terminal OH-groups have been prepared and adequately deprotonated with K[*t*-BuO] in DMSO to act as nucleophiles. UV−vis spectroscopy was used to estimate the number of peripheral cobaltabisdicarbollide units by using the Beer−Lambert Law and confirm the complete functionalization of the starting dendrimeric systems. HPLC indicated slightly different retention times for the functionalized dendrimers depending on the number of cobaltabisdicarbollide units and the core molecule. Because of the anionic character of these compounds and the boron-rich content, we actually focus our research on their biocompatibility studies and potential applications.

Experimental Section

Instrumentation. Melting points were obtained on a Gallenkamp MFB-595 apparatus and are uncorrected. Microanalyses were performed in the analytical laboratory using a Carlo Erba EA1108 microanalyser. FTIR spectra were recorded from KBr pellets on a Perkin-Elmer 16F-PC FTIR and a Shimadzu FTIR-8300 spectrophotometers. The ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on Jeol Eclipse +400, and Bruker ARX 300 spectrometers. The ^{11}B NMR spectra were recorded on a Bruker ARX 300 spectrometer. All NMR spectra were recorded in $CDCl_3$ or CD_3COCD_3 solutions at 25 °C. Chemical shift values for ^{11}B{^{1}H} NMR spectra were referenced to external $BF_3\cdot OEt_2$, and those for ^{1}H and ^{13}C{^{1}H} NMR were referenced to $SiMe_4$. Chemical shifts are reported in units of parts per million downfield from reference, and all coupling constants are reported in hertz (Hz). UV−vis spectra were recorded using a Shimadzu UV-1700 Pharmaspec spectrophotometer, using 1 cm cuvettes, and the concentration of the compounds **5a**, **5b**, **6a**, and **6b** was 1.6×10^{-5} mol·L^{-1} in EtOH at room temperature. MALDI-TOF-MS spectra were recorded in the negative ion mode using a Bruker Biflex MALDI-TOF [N_2 laser; λ_{exc} 337 nm (0.5 ns pulses); voltage ion source 20.00 kV (Uis1) and 17.50 kV (Uis2)].

Materials. All reactions were performed under an atmosphere of dinitrogen employing standard Schlenk techniques. DMSO was purchased from Merck and distilled under standard methods prior to use. Starting materials: potassium carbonate, potassium *tert*-butoxide, DMF, THF, Et_2O, CH_2Cl_2, and acetone were commercially available from Aldrich and used as received. 3,5-Bishydroxymethylphenol,[28] [3,3′-Co(8-$C_4H_8O_2$-1,2-$C_2B_9H_{11}$)-(1′,2′-$C_2B_9H_{11}$)], **4**,[4b,8] and compounds **1a**, **1b**, **2a**, and **2b** were synthesized according to the literature.[22,23]

Synthesis of α,α′-Bis[3,5-bis-[[3,5-bis(hydroxymethyl)phenoxy]-methylen]phenoxy]-*p*-xylene (3a). A mixture of 1.17 g (2.41 mmol) of α,α′-bis[3,5-bis(chloromethyl)phenoxy]-*p*-xylene (**2a**), 1.50 g (9.70 mmol) of 3,5-bishydroxymethylphenol, and 2.60 g (19.30 mmol) of K_2CO_3 in 40 mL of acetone was refluxed for 96 h. The solution was filtered to remove the inorganic salts and evaporated under vacuum. The product was washed with CH_2Cl_2 and ethyl acetate and chromatographed over silica gel eluting with a 9:1 mixture of CH_2Cl_2:MeOH to give 1.80 g (1.88 mmol) of **3a** in 78%. Mp 137−140 °C. IR ν (KBr), 3367, 2869, 1710, 1597, 1456, 1296, 1154, 1020, 846 cm^{-1}. MS-FAB, *m*/*z* (%) [M$^+$, 955 (1)], 460 (7), 393 (33), 366 (100), 349 (40), 322 (47), 307 (43), 279 (35), 209 (22). ^{1}H NMR (399.78 MHz, DMSO-d$_6$) δ: 7.45 (4H, s), 7.11 (2H, s), 7.06 (4H, s), 6.86 (4H, s), 6.83 (8H, s), 5.12 (8H, s), 5.05 (4H, s), 4.45 (16H, s) ppm. ^{13}C NMR (100.52 MHz, DMSO-d$_6$) δ: 159.4, 158.6, 144.5, 139.6, 137.1, 128.4, 119.4, 117.5, 113.7, 111.5, 70.1, 69.9, 63.5.

Synthesis of α,α,′-Bis[3,5-bis-[[3,5-bis(hydroxymethyl)phenoxy]-methylen]phenoxy]-*m*-xylene (3b). A mixture of 2.35 g (4.80 mmol) of α,α′-bis[3,5-bis(chloromethyl)phenoxy]-*m*-xylene (**2b**), 3.00 g (19.40 mmol) of 3.5-bishydroxymethylphenol and 5.37 g (38.90 mmol) of K_2CO_3 in 60 mL acetone was refluxed for 96 h. The solution was filtered to remove the inorganic salts and evaporated under vacuum. The product was washed with CH_2Cl_2 and ethyl acetate and chromatographed over silica gel using a 9:1 mixture of CH_2Cl_2/MeOH to give 3.55 g (3.70 mmol) of **3b** in 77% yield. Mp 94−97 °C. IR ν (KBr), 3290, 2873, 1698, 1597, 1454, 1296, 1150, 1020, 843, 702 cm^{-1}. MS-FAB, *m*/*z* (%) [M$^+$, 954 (5)], 824 (3), 545 (6), 460 (10), 393 (12), 327 (57), 307 (100), 289 (58), 219 (37). ^{1}H NMR (399.78 MHz, DMSO-d_6) δ: 7.56 (1H, s), 7.43 (2H, s), 7.37 (1H, s), 7.12 (2H, s), 7.07 (4H, s), 6.85 (4H, s), 6.83 (8H, s), 5.13 (4H, s), 5.05 (8H, s), 4.44 (16H, s) ppm. ^{13}C NMR (100.52 MHz, DMSO-d_6) δ: 159.1, 158.8, 144.5, 139.6, 137.7, 129.2, 127.9, 127.6, 119.3, 117.4, 113.6, 111.4, 69.8, 69.4, 63.3.

Synthesis of Cs$_4$[5a]. To a solution of **1a** (12.8 mg, 0.03 mmol) in 4 mL of dry DMSO at room temperature was added *t*-BuOK (16.2 mg, 0.15 mmol). The suspension was stirred for 30 min at room temperature. After, compound **4** (51.3 mg, 0.13 mmol) was added and stirred for 24 h. The reaction was quenched by the addition of 1 mL of water and one drop of HCl (1 M). Organic solvents were then evaporated in vacuo to give an orange oily residue, that was dissolved in the minimum volume of ethanol (∼ 1 mL), and 10 mL of an aqueous solution containing an excess of CsCl was added, resulting in the formation of a fine orange suspension. The suspension was taken up with 10 mL of diethyl ether, and the mixture was then transferred to a separatory funnel. The layers were separated, and the organic phase was extracted with additional diethyl ether (2 × 10 mL). Combined diethyl ether fractions were dried over anhydrous $MgSO_4$ and evaporated. The resulted solid was dissolved in CH_2Cl_2−CH_3CN (1:1) and chromatographed on a silica gel plate (25 × 25 cm), eluting with the same solvent mixture to give Cs$_4$[**5a**] as an orange powder. Yield: 41 mg, 51%. IR (KBr, cm^{-1}): 3042 ν(C_c−H), 2971, 2922, 2873 ν(C_{alkyl}−H), 2561 ν(B−H). ^{1}H NMR ((CD$_3$)$_2$CO): 7.53 (s, 4H, C_6H_4), 6.97 (s, 4H, C_6H_3), 6.94 (s, 2H, C_6H_3), 5.14 (s, 4H, OCH_2), 4.56 (s, 8H, OCH_2), 4.23 (br s, 16H, C_c−H), 3.64 (m, 24H, OCH_2), 3.56 (t, 8H, ^3J(H,H) = 6 Hz, OCH_2). ^{1}H{^{11}B} NMR ((CD$_3$)$_2$CO): 7.53 (s, 4H, C_6H_4), 6.97 (s, 4H, C_6H_3), 6.94 (s, 2H, C_6H_3), 5.14 (s, 4H, OCH_2), 4.56 (s, 8H, OCH_2), 4.23 (br s, 16H, C_c−H), 3.64 (m, 24H, OCH_2), 3.56 (t, 8H, ^3J(H,H) = 6 Hz, OCH_2), 2.89 (s, 16H, B−H), 2.75 (s, 8H, B−H), 2.70 (s, 4H, B−H), 2.07 (s, 4H, B−H), 2.02 (s, 8H, B−H), 1.82 (s, 8H, B−H), 1.65 (s, 8H, B−H), 1.55 (s, 8H, B−H), 1.47 (s, 4H, B−H). ^{13}C{^{1}H} NMR ((CD$_3$)$_2$CO): 158.9, 140.7, 140.1, 127.9, 119.0, 112.7, 72.6 (OCH_2), 71.6 (OCH_2), 69.9 (OCH_2), 69.5 (OCH_2), 69.0 (OCH_2), 68.23 (OCH_2), 53.7 (C_c−H), 46.2 (C_c−H). ^{11}B{^{1}H} NMR ((CD$_3$)$_2$CO): 24.7 (s, 4B, B(8)), 5.9 (d, ^1J(B,H) = 121 Hz, 4B), 1.9 (d, ^1J(B,H) = 133 Hz, 4B), −1.0 (d, ^1J(B,H) = 139 Hz, 4B), −2.9 (d, ^1J(B,H) = 162 Hz, 8B), −5.9 (8B), −6.5 (16B), −15.9 (d, ^1J(B,H) = 153 Hz, 8B), −18.9 (d, ^1J(B,H) = 154 Hz, 8B), −20.4 (4B), −27.0 (d, ^1J(B,H) = 113 Hz, 4B). Anal. Calcd. for $C_{66}H_{144}B_{72}Co_4Cs_4O_{12}$: C, 29.63; H, 5.42. Found: C, 28.72; H, 5.55.

Synthesis of Cs$_4$[5b]. The procedure was the same as for Cs$_4$[**5a**], using **1b** (38.4 mg, 0.09 mmol) in 4 mL of DMSO, *t*-BuOK (42 mg, 0.38 mmol) and **4** (156.1 mg, 0.38 mmol). Compound Cs$_4$[**5b**] was isolated as an orange solid. Yield: 149 mg, 62%. IR (KBr, cm^{-1}): 3041 ν(C_c−H), 2957, 2919, 2870 ν(C_{alkyl}−H), 2561 ν(B−H). ^{1}H NMR ((CD$_3$)$_2$CO): 7.62 (s, 1H, C_6H_4), 7.45 (s, 3H, C_6H_4), 6.98 (s, 4H, C_6H_3), 6.93 (s, 2H, C_6H_3), 5.15 (s, 4H, OCH_2), 4.55 (s, 8H, OCH_2), 4.17 (br s, 16H, C_c−H), 3.64 (m, 24H, OCH_2), 3.54 (t, 8H, ^3J(H,H) = 6 Hz, OCH_2). ^{1}H{^{11}B} NMR ((CD$_3$)$_2$CO): 7.53 (s, 4H, C_6H_4), 6.97 (s, 4H, C_6H_3), 6.94 (s, 2H, C_6H_3), 5.14 (s, 4H, OCH_2), 4.56 (s, 8H, OCH_2), 4.23 (br s, 16H, C_c−H), 3.64 (m, 24H, OCH_2), 3.56 (t, 8H, ^3J(H,H) = 6 Hz, OCH_2), 2.91 (s, 16H, B−H), 2.74 (s, 8H, B−H), 2.70 (s, 4H, B−H), 2.02 (s, 8H,

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B−H), 1.83 (s, 8H, B−H), 1.69 (s, 4H, B−H), 1.63 (s, 8H, B−H), 1.54 (s, 8H, B−H), 1.44 (s, 4H, B−H). $^{13}C\{^1H\}$ NMR ($(CD_3)_2CO$): 159.0, 140.2, 137.9, 128.6, 126.82, 124.7, 119.4, 113.0, 72.2 (OCH_2), 71.8 (OCH_2), 69.8 (OCH_2), 69.5 (OCH_2), 69.2 (OCH_2), 68.2 (OCH_2), 53.3 (C_c−H), 46.2 (C_c−H). $^{11}B\{^1H\}$ NMR ($(CD_3)_2CO$): 24.5 (s, 4B, B(8)), 5.9 (d, ^1J(B,H) = 125 Hz, 4B), 1.3 (d, ^1J(B,H) = 134 Hz, 4B), −1.6 (d, ^1J(B,H) = 139 Hz, 4B), −3.6 (d, ^1J(B,H) = 173 Hz, 8B), −6.3, (8B), −6.5 (16B), −16.4 (d, ^1J(B,H) = 152 Hz, 8B), −19.6 (d, ^1J(B,H) = 156 Hz, 8B), −20.8 (4B), −27.6 (d, ^1J(B,H) = 124 Hz, 4B). Anal. Calcd. for $C_{66}H_{144}B_{72}Co_4Cs_4O_{12}$: C, 29.63; H, 5.42. Found: C, 28.30; H, 5.39.

Synthesis of Cs_8[6a]. The procedure was the same as for Cs_4[**5a**], using **3a** (12.7 mg, 0.013 mmol) in 6 mL of DMSO, *t*-BuOK (13.51 mg, 0.120 mmol) and **4** (53.7 mg, 0.131 mmol). Compound Cs_8[**6a**] was isolated as an orange solid. Yield: 28 mg, 41%. IR (KBr, cm^{-1}): 3040 ν(C_c−H), 2959, 2920, 2862 ν(C_{alkyl}−H), 2558 ν(B−H). ^1H NMR ($(CD_3)_2CO$): 7.55 (s, 4H, C_6H_4), 7.22 (s, 2H, C6H3), 7.16 (s, 4H, C_6H_3), 7.02 (s, 4H, C_6H_3), 6.99 (s, 8H, C_6H_3), 5.18 (s, 4H, OCH_2), 5.13 (s, 8H, OCH_2), 4.55 (s, 16H, OCH_2), 4.15 (br s, 32H, C_c−H), 3.64 (m, 48H, OCH_2), 3.54 (t, 16H, ^3J(H,H) = 6 Hz, OCH_2). $^1H\{^{11}B\}$ NMR ($(CD_3)_2CO$): 7.55 (s, 4H, C_6H_4), 7.22 (s, 2H, C_6H_3), 7.16 (s, 4H, C_6H_3), 7.02 (s, 4H, C_6H_3), 6.99 (s, 8H, C_6H_3), 5.18 (s, 4H, OCH_2), 5.13 (s, 8H, OCH_2), 4.55 (s, 16H, OCH_2), 4.15 (br s, 32H, C_c−H), 3.64 (m, 48H, OCH_2), 3.54 (t, 16H, ^3J(H,H) = 6 Hz, OCH_2), 2.88 (s, 32H, B−H), 2.74 (s, 16H, B−H), 2.70 (s, 8H, B−H), 2.03 (s, 16H, B−H), 1.84 (s, 16H, B−H), 1.68 (s, 8H, B−H), 1.63 (s, 16H, B−H), 1.54 (s, 16H, B−H), 1.44 (s, 8H, B−H). $^{13}C\{^1H\}$ NMR ($(CD_3)_2CO$): 159.7, 159.1, 140.3, 135.0, 129.5, 127.81, 119.7, 113.3, 72.5 (OCH_2), 72.2 (OCH_2), 71.9 (OCH_2), 70.0 (OCH_2), 69.7 (OCH_2), 69.4 (OCH_2), 68.4 (OCH_2), 53.2 (C_c−H), 46.5 (C_c−H). $^{11}B\{^1H\}$ NMR ($(CD_3)_2CO$): 24.6 (s, 8B, B(8)), 6.5 (d, ^1J(B,H) = 120 Hz, 8B), 1.9 (d, ^1J(B,H) = 135 Hz, 8B), −1.6 (d, ^1J(B,H) = 130 Hz, 8B), −2.6(d, ^1J(B,H) = 180 Hz, 16B), −6.3, (16B), −6.8 (32B), −16.4 (d, ^1J(B,H) = 150 Hz, 16B), −19.7 (d, ^1J(B,H) = 151 Hz, 16B), −20.8 (8B), −27.6 (d, ^1J(B,H) = 120, 8B). Anal. Calcd. for $C_{141}H_{294}B_{144}Co_8Cs_8O_{26}$: C, 30.51; H, 5.39. Found: C, 29.50; H, 5.20.

Synthesis of Cs_8[6b]. The procedure was the same as for Cs_4[**5a**], using **3b** (29.0 mg, 0.030 mmol) in 6 mL of DMSO, *t*-BuOK (34.2 mg, 0.264 mmol) and **4** (108 mg, 0.263 mmol). Compound Cs_8[**6b**] was isolated as an orange solid. Yield: 75 mg, 47%. IR (KBr, cm^{-1}): 3043 ν(C_c−H), 2952, 2921, 2869 ν(C_{alkyl}−H), 2562 ν(B−H). ^1H NMR ($(CD_3)_2CO$): 7.62 (s, 1H, C_6H_4), 7.45 (s, 3H, C_6H_4), 7.22 (s, 2H, C_6H_3), 7.15 (s, 4H, C_6H_3), 7.02 (s, 4H, C_6H_3), 6.98 (s, 8H, C_6H_3), 5.19 (s, 4H, OCH_2), 5.13 (s, 8H, OCH_2), 4.55 (s, 16H, OCH_2), 4.13−4.09 (br s, 32H, C_c−H), 3.64 (m, 48H, OCH_2), 3.54 (m, 16H, OCH_2). $^1H\{^{11}B\}$ NMR ($(CD_3)_2$-CO): 7.62 (s, 1H, C_6H_4), 7.45 (s, 3H, C_6H_4), 7.22 (s, 2H, C_6H_3), 7.15 (s, 4H, C_6H_3), 7.02 (s, 4H, C_6H_3), 6.98 (s, 8H, C_6H_3), 5.19 (s, 4H, OCH_2), 5.13 (s, 8H, OCH_2), 4.55 (s, 16H, OCH_2), 4.13−4.09 (br s, 32H, C_c−H), 3.64 (m, 48H, OCH_2), 3.54 (m, 16H, OCH_2), 2.88 (s, 32H, B−H), 2.70 (s, 24H, B−H), 2.03 (s, 16H, B−H), 1.83 (s, 16H, B−H), 1.68 (s, 8H, B−H), 1.62 (s, 16H, B−H), 1.53 (s, 16H, B−H), 1.44 (s, 8H, B−H). $^{13}C\{^1H\}$ NMR ($(CD_3)_2CO$): 159.1, 140.3, 139.3, 137.6, 128.7, 127.2, 119.8, 119.12, 113.4, 72.8 (OCH_2), 72.5 (OCH_2), 72.0 (OCH_2), 70.0 (OCH_2), 69.7 (OCH_2), 69.4 (OCH_2), 68.4 (OCH_2), 53.1 (C_c−H), 46.6 (C_c−H). $^{11}B\{^1H\}$ NMR ($(CD_3)_2CO$): 24.8 (s, 8B, B(8)), 6.5 (d, ^1J(B,H) = 125 Hz, 8B), 1.5 (d, ^1J(B,H) = 134 Hz, 8B), −1.5 (d, ^1J(B,H) = 131 Hz, 8B), −3.9 (d, ^1J(B,H) = 160 Hz, 16B), −6.1, (48B), −16.2 (d, ^1J(B,H) = 141 Hz, 16B), −19.3 (d, ^1J(B,H) = 153 Hz, 16B), −20.4 (8B), −27.4 (d, ^1J(B,H) = 111 Hz, 8B). Anal. Calcd. for $C_{141}H_{294}B_{144}Co_8Cs_8O_{26}$: C, 30.51; H, 5.39. Found: C, 29.27; H, 5.63.

HPLC. The chromatographic Agilent Hewlett-Packard 1100 system consist of a HP 1100 pump, HP 1100 UV−vis detector and HP ChemStation integrator. Retention time measurements were carried out on a Nucleosil 5 C18-AB, 150 mm × 4.6 m, 5 μm particle size reverse phase column at 22 °C. The samples were introduced through a Rheodyne injector valve with the 20 μL sample loop. The UV detector was fixed at 310 nm of wavelength. The chromatographic method for separation of these compounds used a mobile phase of pure methanol, and the flow rate was 1 mL/min. The sample concentrations were $3.2 \times 10-5$ M in all cases.

Single Crystal X-ray Structure Determinations. X-ray data were collected on an Enraf Nonius FR590 diffractometer with a CCD area detector equipped with a graphite monochromator, $\lambda_{(MoK\alpha)}$ = 0.710 73 Å. The data set was recorded at 293 K in ω/φ-scan mode. The structure was solved by SIR-2004[29] and refined by the full-matrix least-squares methods with SHELXL-97.[30] All manipulations were done under the package WingGX-Version 1.80.05.[31] All non-hydrogen atoms were refined anisotropically. C−H hydrogen atoms were placed in geometrically calculated positions using a riding model. Crystallographic data for compound **2a** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications No. CCDC 782355. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax, (+44)1223−336−033; e-mail, deposit@ccdc.cam.ac.uk; web-site, http://www.ccdc.cam.ac.uk).

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Supporting Information Available: Further details of data collection and structure refinement, and ^1H, $^{13}C\{^1H\}$ NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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