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High-Boron-Content Porphyrin-Cored Aryl Ether Dendrimers: Controlled Synthesis, Characterization, and Photophysical Properties

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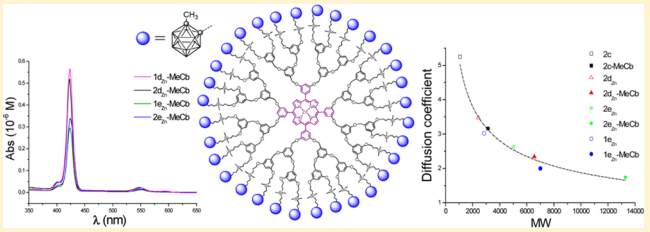
Supporting Information

ABSTRACT: The synthesis and characterization of a set of poly(aryl ether) dendrimers with tetraphenylporphyrin as the core and 4, 8, 16, or 32 *closo*-carborane clusters are described. A regioselective hydrosilylation reaction on the allyl-terminated functions with carboranylsilanes in the presence of Karstedt's catalyst leads to different generations of boron-enriched dendrimers. This versatile approach allows the incorporation of a large number of boron atoms in the dendrimers' periphery. Translational diffusion coefficients (D) determined by DOSY NMR experiments permit estimation of the hydrodynamic radius (R_H) and molecular size for each dendrimer. Furthermore, a notable correlation between D and the molecular weight (MW) is found and can be used to predict their overall size and folding properties. The UV−vis and emission behavior are not largely affected by the functionalization, therefore implying that the presence of carboranes does not alter their photoluminescence properties.



INTRODUCTION

Dendrimers are treelike branched polymers with low polydispersity and a high degree of versatility that tend to adopt globular structures with a well-defined three-dimensional shape.[1] Since the first synthesis reported by Tomalia et al.,[2] these materials have attracted the attention of many research groups because they can be built in a controlled manner, allowing versatility in the nucleus, branching units, or dendrons as well as in the terminal groups.[3] This allows one to change the properties of dendrimers and also to modulate their behavior, with the goal centered on the design and synthesis of dendrimers more specific for certain areas,[4] such as carriers for drug delivery.[5,6] For all of these reasons, they emerged as a new appealing class of particles for nanomedicine.[7] In this respect, boron-enriched dendrimers have been developed for different groups as boron carriers for boron neutron capture therapy (BNCT).[8−10] Our group has also contributed to the search of synthetic strategies for the preparation of high-boron-content neutral dendrimeric systems that incorporate *closo*-carboranes[11,12] and water-soluble polyanionic dendrimers bearing *nido*-carborane[13−15] as well as metallodendrimers containing cobaltabis(dicarbollide) fragments.[16−18] As is well-known, icosahedral carborane derivatives have recently attracted much attention in biomedical and medicinal applications because of their extraordinary characteristics.[19] The hydrophobic character of carboranes can enhance the interactions between pharmaceuticals and their receptors,[20−24] and they have been extensively involved in areas of drug discovery, such as pharmacophores and biologically active compounds.[25−28] During the last decades, several boron-containing porphyrins, with *closo*-carborane[29,30] and *nido*-carborane,[31] have been synthesized and evaluated in vitro and in vivo as promising BNCT agents.[32−35] The combined action of a porphyrin used as a core with dendrons of poly(aryl ether) for the synthesis of dendrimers was first reported by Inoue and collaborators.[36] By using Fréchet's methodology, they prepared an iron porphyrin covalently encapsulated within a large aryl ether dendrimer cage as the first monomolecular model of hemoproteins.[37]

On the basis of both the biocompatibility of porphyrin-cored poly(aryl ether) dendrimers[38−42] and the bioactivity of carborane-containing molecules,[21] in this work our goal is the synthesis and characterization of dendrimers that contain a large number of carborane clusters, in order to obtain biocompatible boron-rich molecules. Synthetic aspects as well as a complete characterization of free-base and zinc-metalated porphyrin-cored dendrimers before and after the incorporation of *closo*-carboranes are discussed. The molecular sizes for these

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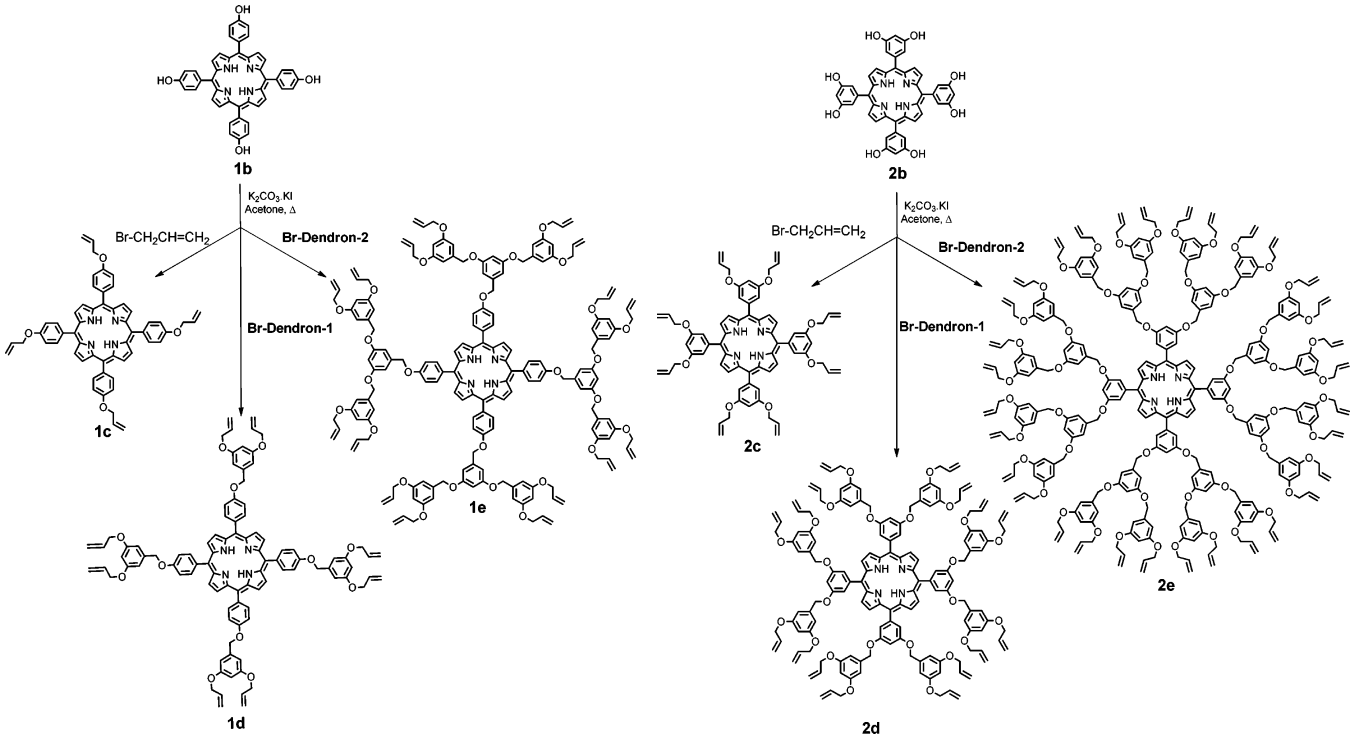
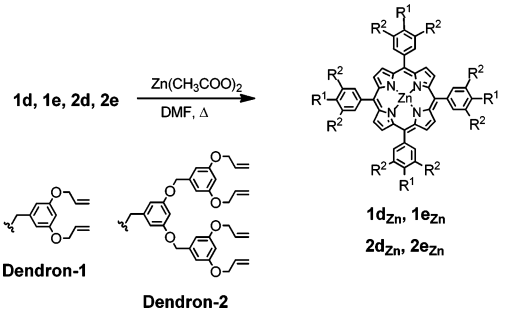
Scheme 1. Route of the Preparation of Dendrimers 1c−1e and 2c−2e



Scheme 2. Metalation of the Porphyrin Core of Dendrimers 1d−1e and 2d−2e with Zinc(II)



Compound	R^1	R^2
$1d_{Zn}$	Dendron-1	H
$1e_{Zn}$	Dendron-2	H
$2d_{Zn}$	H	Dendron-1
$2e_{Zn}$	H	Dendron-2

kinds of dendrimers were estimated before and after the incorporation of carborane clusters from their hydrodynamic radii (R_H), which were determined using translational diffusion coefficients (D) from DOSY NMR experiments. A comparative study of the absorption and emission properties for all compounds has been carried out, and the influence of the cluster attached to the dendrimer periphery on these photophysical properties has been investigated. We currently focus our research on the study of the biocompatibility and cytotoxicity of these dendrimers for potential biomedical applications.

RESULTS AND DISCUSSION

Synthesis of Carboranyl-Containing Porphyrin-Cored Dendrimers. Different generations of poly(aryl ether) dendrimers with terminal allyl ether groups and a porphyrin as the core have been used as a platform to prepare high-boron-content macromolecules after functionalization with carboranyl fragments. The preparation of the porphyrin macrocycles **1a**[43] and **2a**[44] was carried out from *p*-methoxybenzaldehyde or 3,5-dimethoxybenzaldehyde in the presence of pyrrole and propionic acid as a reaction medium (see the Supporting Information, SI).[45,46] After demethylation with HBr and CH_3COOH,[47] porphyrin cores **1b**[48] and **2b**[49] were obtained (see the SI). On the other hand, Fréchet dendron types, **Br-dendron-1** and **Br-dendron-2**, with allyl groups at the periphery were prepared by esterification of 3,5-dihydroxybenzoic acid in methanol and H_2SO_4, followed by coupling with allyl bromide in the presence of K_2CO_3, KI, and acetone. The subsequent reduction of the ester with $LiAlH_4$ in tetrahydrofuran gave benzylic alcohol, which was treated with $SOCl_2$ and pyridine to generate **Br-dendron-1**.[50−53] From the reaction of 3,5-dihydroxybenzylic alcohol and **Br-dendron-1**, a second derivative of benzylic alcohol was obtained and submitted to a second halogenation to give **Br-dendron-2**.[54,55] The spectroscopic data for dendrons and intermediates are in agreement with those reported in the literature. The reaction of porphyrins **lb** or **2b** with allyl bromide, **Br-dendron-1**, or **Br-dendron-2** in acetone in the presence of K_2CO_3 and KI leads to the formation of dendrimers with 4 (**1c**),[56] 8 (**1d** and **2c**), 16 (**1e** and **2d**), and 32 (**2e**) allyl groups at the periphery (Scheme 1). Likewise, metalation of the porphyrins in the dendrimers was carried out using *N*,*N*-dimethylformamide (DMF) and $Zn(CH_3COO)_2{\cdot}2H_2O$ (Scheme 2).[46] With

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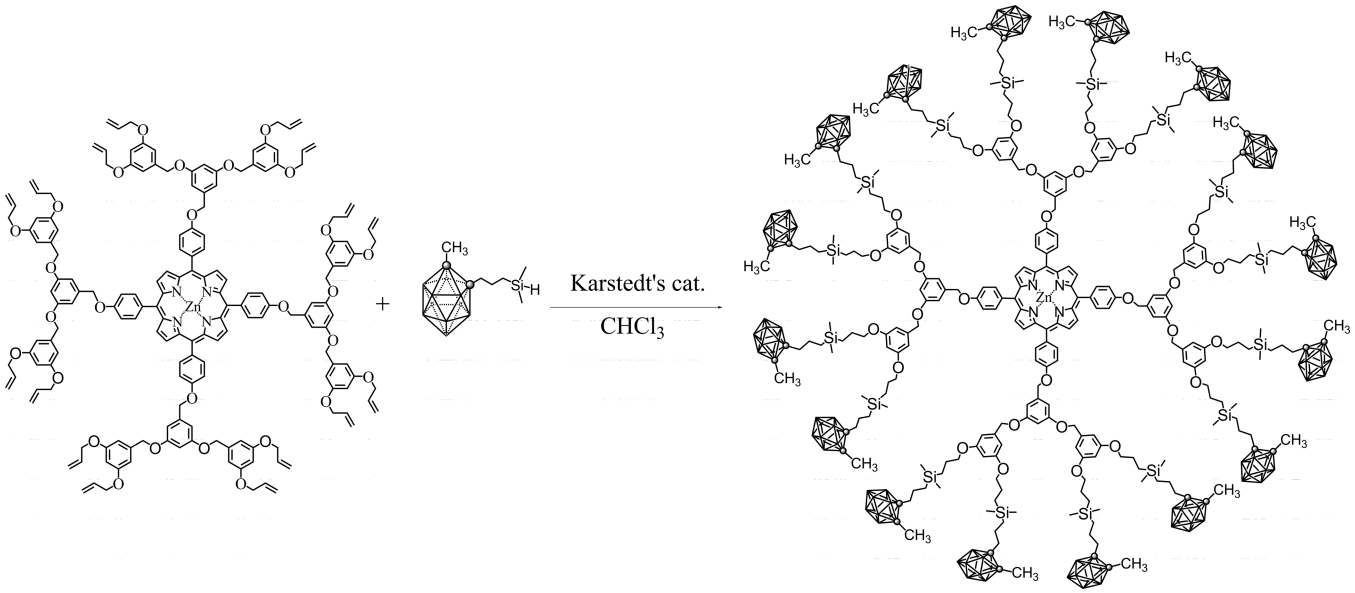
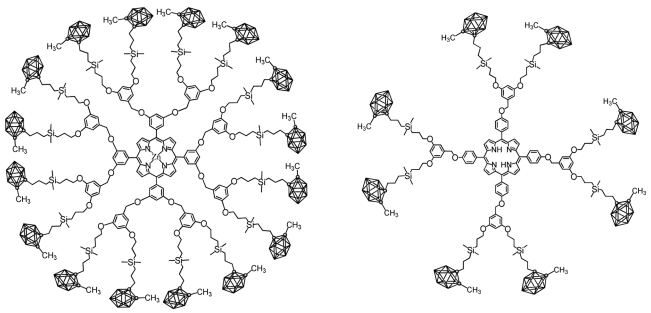
Scheme 3. Hydrosilylation Reaction To Obtain Dendrimer $1e_{Zn}$-MeCb



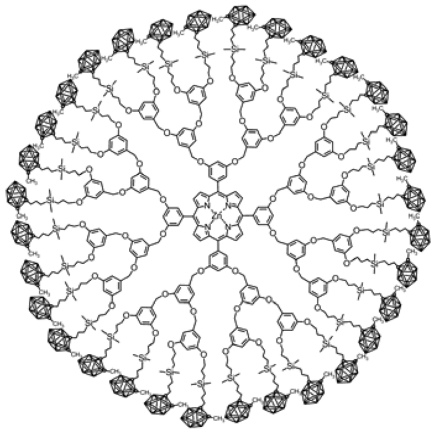
the aim of obtaining high-boron-rich porphyrin-cored dendrimers, we have selected some of these dendritic structures, either free base or zinc porphyrins, to be functionalized with carboranyl derivatives via catalytic hydrosilylation reactions. This approach has already been used before by our group and represents a versatile and efficient methodology to introduce a large number of boron atoms into a molecule.[15] The carboranylsilane 1-CH_3-2-[$CH_2CH_2CH_2(CH_3)_2SiH$]-1,2-*closo*-$C_2B_{10}H_{10}$ was used as the hydrosilylating agent; this is a suitable choice because this precursor is obtained in a fast way and with high yield and has shown to be very efficient in previous hydrosilylation reactions.[12]

To functionalize the periphery of the different generations of porphyrin-cored dendrimers, hydrosilylation reactions of the terminal allyl groups with carboranylsilane were carried out. All reactions were catalyzed by Karstedt's catalyst[57] with the purpose of controlling the regioselectivity of the reaction to obtain the desired β isomers (Scheme 3). Nevertheless, for the different dendrimers, a large number of experiments were performed to find the optima and specific conditions in terms of the stoichiometry, solvent, temperature, and time of reaction. The synthesis of compound **1c-MeCb** (see Figure S1 in the SI) was performed in a minimum volume of CH_2Cl_2, while the syntheses of **1d-MeCb** (Figure 1) and **$1d_{Zn}$-MeCb** were carried out in $CHCl_3$ using a ratio of dendrimer/hydrosilylating agent of 1:1.5 at 50 °C for 5 h in the presence of Karstedt's catalyst (see Scheme 3 as an example of the synthesis of **$1e_{Zn}$-MeCb**). In the case of compound **2c-MeCb**, a higher ratio of carboranylsilane, 1:2, was necessary. To prepare higher generations of dendrimers, **$1e_{Zn}$-MeCb**, **$2d_{Zn}$-MeCb**, and **$2e_{Zn}$-MeCb** (see Figure 1), 1,4-dioxane was used as the solvent because the starting dendrimers were not soluble or the reaction did not work well in other solvents, allowing an increase of the temperature. Besides, a higher ratio of carboranylsilane corresponding to a 100% excess was required for complete hydrosilylation of all terminal allyl groups (16 or 32; Scheme 3).

Hydrosilylation reactions were monitored by ^{1}H NMR spectroscopy to determine completion of the reaction upon the disappearance of the allyl proton resonances of the starting



$2d_{Zn}$-MeCb **1d-MeCb**



$2e_{Zn}$-MeCb

Figure 1. Structural representation of some carboranyl-containing porphyrin-cored dendrimers.

dendrimers; also important is monitoring of the O−CH_2 resonance (H-15 in Figure 2) because after functionalization the signal is shifted to lower frequencies. The preparation of pure compounds is a requirement for the development of compounds especially for biological applications. Therefore, because of the presence of Karstedt's catalyst, a further purification of the functionalized molecules by thin-layer

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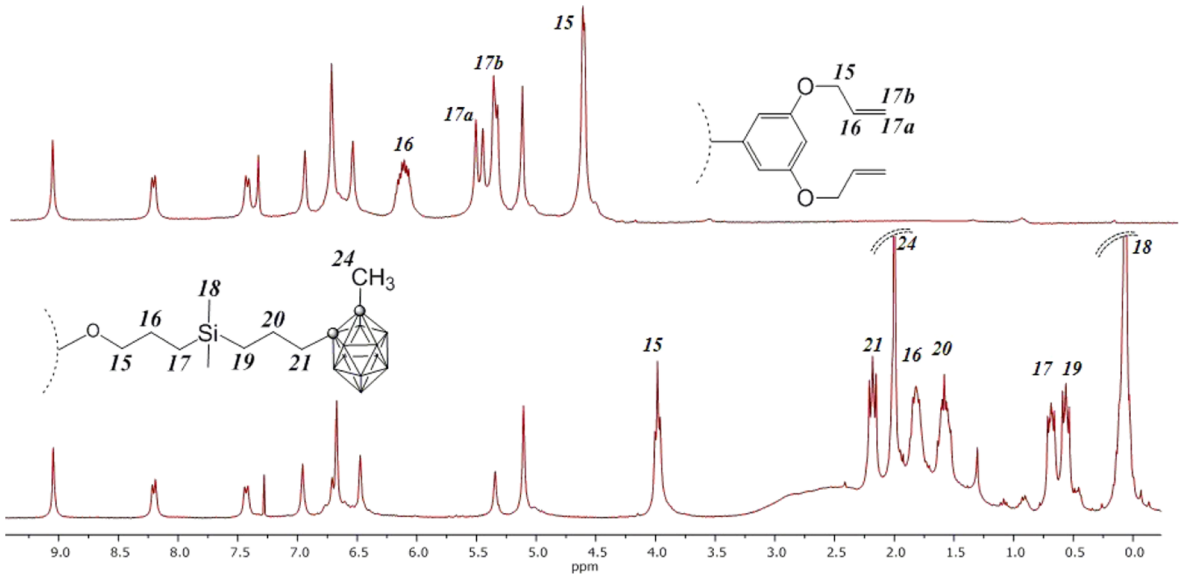

Figure 2. ^{1}H NMR spectra of dendrimer **1e$_{Zn}$-MeCb** before and after functionalization with carborane clusters.

chromatography (TLC) was necessary. This made it possible to recover almost all of the excess carboranylsilane used in the reactions. After that, all carboranyl-containing dendrimers were isolated in excellent yields, in the range 60−88%. Remarkably, reactions with zinc porphyrin cored dendrimers gave higher yields after functionalization with the carboranylsilanes than those from metal-free porphyrins. Indeed, some metal-free porphyrin dendrimer derivatives could not be fully functionalized; however, this could be achieved for the metalated cores. This may be due to coordination of the catalyst to the porphyrinic nitrogen atoms, which produces their partial deactivation.

Characterization of Carboranyl-Containing Porphyrin-Cored Dendrimers. The starting dendrimers were characterized by ^{1}H and ^{13}C NMR, electrospray ionization (ESI-MS), and the signals were assigned from two-dimensional (2D) HSQC experiments. The ^{1}H NMR spectra showed signals assigned to the core (H-β) and NH from 8.85 to 9.00 ppm and from −2.69 to −2.87 ppm, respectively; these NH signals disappear in the corresponding dendrimers with the zinc core, and the allylic signals appear in the range from 5.16 to 6.25 ppm. Likewise, the ^{13}C NMR spectra show signals at 131.2−133.2 ppm (C-β) and 119.9−120.9 ppm (*meso*-C) corresponding to the core. The signals for the allyl groups appear at 69.0−70.5 ppm (CH_2), 133.2−133.6 ppm ($CH{=}CH_2$), and 117.9−118.2 ppm ($CH{=}CH_2$). The structures of carboranyl-containing dendrimers were established by IR, ^{1}H, ^{13}C{^{1}H}, ^{11}B, and ^{11}B{^{1}H} NMR, and elemental analysis. The IR spectra of the carboranyl-containing dendrimers show the typical ν(B−H) strong bands for *closo* clusters around 2580 cm^{-1}. The absence of a band at 2112 cm^{-1} corresponding to ν(Si−H) from the silane function of the carboranylsilane indicates the total hydrosilylation of the alkene. In the ^{1}H NMR spectra, resonances in the range of 6.25−5.16 ppm due to the allyl protons have disappeared after hydrosilylation reaction, confirming anti-Markovnikov addition of the μ-SiH function to the double bonds and, subsequently, complete peripheral functionalization. In the latter compounds, the presence of new proton resonances in the $-CH_2-$ region corroborates their formation. These resonances correspond to protons H-6 and H-7 in first-generation dendrimers, H-11 and H-12 in the second-generation dendrimers, and H-16 and H-17 in the third-generation dendrimers (see the SI). The ^{1}H NMR spectra for dendrimers bearing *closo* clusters also exhibit resonances at low frequencies, in the −0.11 to −0.08 ppm range for Si-CH_3 protons. In addition, all nonmetalated dendrimers show one resonance near −2.70 ppm due to the two NH protons of the porphyrinic core. The ^{13}C{^{1}H} NMR spectra show resonances attributed to the aromatic signal of the dendron, from 160.5 to 100.0 ppm for all compounds. After functionalization with carboranes, dendrimers show resonances in the region from 84.0 to 74.6 ppm attributed to $C_{cluster}$. The resonances for the Si−CH_3 units bonded to C_c appear around −3.5 ppm, whereas the $-CH_2-$ carbon atoms are displayed in the range from 40.0 to 10.0 ppm.

The ^{11}B{^{1}H} NMR resonances for dendrimers decorated with clusters appear in the characteristic *closo* region, from −6.0 to −11.0 ppm, showing broad overlapped bands with the patterns 2:8. Different mass spectrometry techniques [ESI and matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF)] were also used for characterization of the starting compounds. The formulas of the smaller dendrimers were well established by using ESI-MS showing the molecular ion peak; nevertheless, for the largest dendrimers, neither the ESI nor the MALDI-TOF mass spectra were useful, as important fragmentation was observed. A similar fragmentation had been previously observed for other boron-containing large molecules.[15,17,18]

Experimental Diffusion Coefficients and Estimated Hydrodynamic Radius of Dendrimers. Diffusion NMR experiments have been used to get an estimation of the overall molecular size of a set of six porphyrin-cored aryl ether dendrimers. We have compared dendrimers of different generations before and after functionalization with carboranes (**2c**, **2c-MeCb**, **2d$_{Zn}$**, **2d$_{Zn}$-MeCb**, **2e$_{Zn}$**, and **2e$_{Zn}$-MeCb**). To our knowledge, these are the first boron cluster-containing dendrimers characterized by this technique. Diffusion experiments are displayed using a DOSY (Diffusion-Ordered NMR SpectroscopY) representation, where the chemical shift is plotted versus the diffusion coefficient (D) in a 2D map.[58−60] In addition, diffusion experiments have the advantage of allowing measurement of the diffusion coefficient and

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estimation of the hydrodynamic radius (R_H) according to the Stokes−Einstein equation over a wide range of molecular weights (MW),[61] being a complementary tool to confirm the successful functionalization of our dendrimers. Figure 3 shows

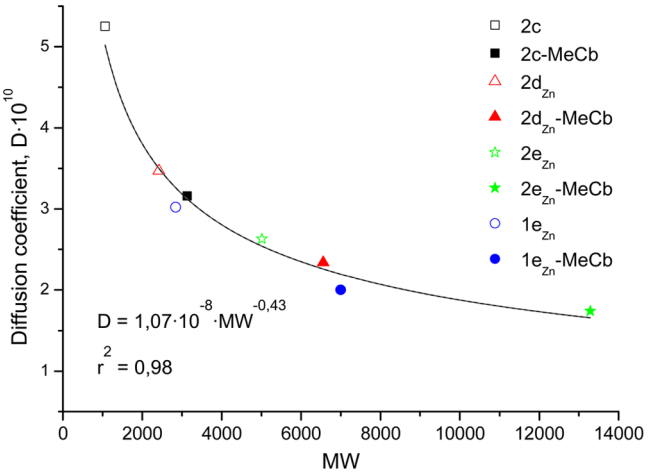

Figure 3. Diffusion coefficients (D) from DOSY experiments versus molecular weights (MW).

the experimental D values of dendrimers as a function of their MW values. The strong correlation between D and MW of the different dendrimers is remarkable, with a rough experimental dependence according to

$$D_A/D_B = (MW_B/MW_A)^a \quad (1)$$

where $a \sim 0.4-0.5$. The simple correlation between D and MW allows for the determination of a calibration curve that could also be applied to a wide range of related compounds under the same conditions of temperature and solvent. To prove this, we have run additional DOSY experiments for dendrimers **1e$_{Zn}$** and **1e$_{Zn}$-MeCb**, which have shown that their D values fit well in the calibration curve (Table 1 and Figure 3). The

Table 1. Diffusion Coefficients and Hydrodynamic Radii Determined by DOSY Experiments for Eight Different Dendrimers

dendrimer	molecular weight (MW)	diffusion coefficient (D)	hydrodynamic radii (R_H, Å)
2c	1063.3	5.25×10^{-10}	7.67
2c-MeCb	3131.1	3.16×10^{-10}	12.7
2d$_{Zn}$	2420.9	3.47×10^{-10}	11.6
2d$_{Zn}$-MeCb	6559.9	2.34×10^{-10}	17.2
2e$_{Zn}$	5014.0	2.63×10^{-10}	15.3
2e$_{Zn}$-MeCb	13290.7	1.74×10^{-10}	23.2
1e$_{Zn}$	2845.1	3.02×10^{-10}	13.3
1e$_{Zn}$-MeCb	6999.4	2.00×10^{-10}	20.2
$CDCl_3$		2.51×10^{-9}	1.60

corresponding R_H values have been calculated assuming that dendrimers are spherical (Table 1). Thus, when R_H for each generation of dendrimer is compared before and after functionalization, it is observed that the R_H value is higher for those dendrimers containing carborane clusters. Obviously, the estimated R_H values also enlarge in a consistent manner when the dendrimer generation is increased. As a general trend, it is observed that full functionalization implies an average increase of the MW by a factor about 2.5−3, a decrease of D by ∼60−65%, and an increase of the estimated R_H by ∼50−60%. The hydrodynamic radii (R_H) values from this work are in good agreement with the sole result on these parameters obtained for phenyl-terminated porphyrin-cored aryl ether dendrimers from other methodology (global analysis of the fluorescence anisotropy decay).[62] It has been reported that the D value of a given known species or the MW from an unknown compound can be roughly predicted based on the relationship

$$\log(D) = a \log(MW) + b \quad (2)$$

where a and b are two coefficients that depend on the solvent and sample concentration with average values of about $a = -0.62$ and $b = -7.49$ for a $CDCl_3$ solution.[63] In general, eq 2 works well for the smaller dendrimers and shows some deviations for the larger ones, which is attributed to a major relative degree of molecular folding. This is in agreement with our experimental data represented in the curve of Figure 3.

Photophysical Properties of Dendrimers. The UV−vis spectra in $CHCl_3$ of the starting dendrimers are similar to those in tetraphenylporphyrin (TPP),[64] with a maximum absorption for the Soret band from 422 to 423 nm, which is red-shifted by 1−2 nm when the core is metalated (Figure S3 in the SI and Table 2). They show molar extinction coefficients (ε) between

Table 2. Absorption Data of Dendrimers before and after Functionalization with Carborane Clusters

dendrimer	$\varepsilon \times 10^{-5}$	λ Soret band	Q_1 band	Q_2 band
1c	3.43	422	519	556
1d	3.43	423	519	556
1e	3.63	423	519	559
2c	3.80	422	515	548
2d	2.40	423	516	552
2e	2.68	423	517	553
1d$_{Zn}$	4.30	423	550	
1e$_{Zn}$	2.61	424	551	
2d$_{Zn}$	3.03	423	549	
2e$_{Zn}$	3.32	425	550	
1c-MeCb	4.97	423	519	556
1d-MeCb	3.49	422	513	550
2c-MeCb	2.52	422	514	550
2d$_{Zn}$-MeCb	5.18	423	547	
1e$_{Zn}$-MeCb	9.50	424	550	
2e$_{Zn}$-MeCb	3.38	424	550	
1d$_{Zn}$-MeCb	5.64	423	551	

2.40×10^5 and 4.30×10^5 M. Typical Q bands were also observed in all starting dendrimers: the Q_1 band was observed from 515 to 519 nm for free-base porphyrin dendrimers, whereas for metalated porphyrin dendrimers, this band appears between 549 and 551 nm, which is around 33 nm red-shifted (Table 2). As is usual, the Q_2 band was only observed for nonmetalated porphyrin dendrimers, in the range from 548 to 559 nm. The excitation and emission spectra of starting dendrimers in $CHCl_3$ are similar to isolated base-free TTP and zinc tetraphenylporphyrin (Table 3 and Figure 4). When free-base porphyrin dendrimers were irradiated at 422 nm, high-intensity emission bands of around 650−658 nm were observed in the emission spectra, whereas other bands of lower intensity were found to be close to 720 nm. On the other hand, for zinc-metalated porphyrin dendrimers, the emission maximum bands are those of low energy at around 650 nm, while the emission bands near 600 nm exhibit lower intensity. The UV−vis

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Table 3. Emission Data of Dendrimers before and after Functionalization with Carborane Cages

dendrimer	λ_{max} Em 1	λ_{max} Em 2
1c	657	724
1d	657	723
1e	658	724
2c	650	715
2d	651	716
2e	650	717
1d$_{Zn}$	602	649
1e$_{Zn}$	602	650
2d$_{Zn}$	596	645
2e$_{Zn}$	601	646
1c-MeCb	657	711
1d-MeCb	656	711
2c-MeCb	649	704
2d$_{Zn}$-MeCb	596	643
1e$_{Zn}$-MeCb	604	644
2e$_{Zn}$-MeCb	599	641
1d$_{Zn}$-MeCb	603	645

absorption and emission spectra of carboranyl-containing porphyrin-cored dendrimers in $CHCl_3$ are shown in Figures 5 and 6, respectively. The UV−vis absorption spectra of carboranyl-functionalized dendrimers are similar to those of the noncarboranyl functionalized ones with Soret bands at 422−424 nm, Q_1 bands at 514−550 nm, and Q_2 bands at 550−556 nm, in some cases blue-shifted by 1−6 nm (see Table 2). Neither the Soret nor the Q bands undergo major changes upon an increase in the dendrimer generation or the number of boron clusters on the periphery. Nevertheless, the zinc porphyrin cored dendrimers exhibit absorption maxima at around 423−424 nm, and a small red shift of ∼1−2 nm of the Soret band is observed as the generation number increases. This effect is typical for these kinds of porphyrin-cored dendrimers, for which Aida et al. suggested that the red shift is associated with the encapsulation degree of the porphyrin into the dendrimer,[65] whereas Fréchet et al. proposed that the red shift of the Soret band is an indication of weak interactions between the core and branches.[62] If we compare the emission spectra of carboranyl-containing dendrimers with the unmodified one, it is noticed that no remarkable differences are observed. For nonmetalated dendrimers, emission maxima are observed between 649 and 657 nm, whereas for zinc porphyrin cored dendrimers, two emission bands are observed, with maxima in the range of 596−604 nm, 4−5 nm blue-shifted with respect to the starting dendrimers (Table 3). As was expected, the encapsulation of emitting porphyrins using poly(aryl ether) dendritic structures does not cause an enhancement of their luminescent properties. In the dendrimers reported here, the size of the dendrimer framework has little influence on the fluorescence properties of the core porphyrins,[66] and the fact that the carboranyl-containing dendrimers show a behavior similar to that of the starting ones without boron clusters indicates that the presence of the peripheral carborane units does not have a major influence on the photophysical properties of the porphyrin core.

CONCLUSIONS

A set of new boron-enriched porphyrin-cored aryl ether dendrimers have been obtained by regioselective hydrosilylation of allyl terminal groups with the adequate carboranylsilane. The synthesis of these dendrimers is highly controlled, and the reaction conditions are optimized for each one. Dendrimers have been fully characterized by IR and NMR spectroscopy as well as elemental analysis. In addition, the diffusion coefficients (D) of some dendrimers before and after functionalization with carborane derivatives have been determined by DOSY experiments, and the hydrodynamic radius (R_H) has been calculated using the Stokes−Einstein equation. A notable correlation between D and MW of dendrimers has been found that can be extrapolated to a wide range of related compounds under the same conditions of temperature and solvent to predict their overall size and folding properties. This technique can be used as a complementary tool to confirm the successful functionalization of our dendrimers with carboranes and could possibly be extended to other functionalities. The UV−vis spectra show the characteristic Soret and Q bands for the porphyrin, which are not largely affected by the dendritic branches or the number of carborane clusters. The emission behavior, before and after functionalization of dendrimers, indicates that there are no changes in the photoluminescence (PL) properties after the incorporation of cages, so that the introduction of carborane clusters to the dendrimeric skeleton does not alter their PL behavior, a facet

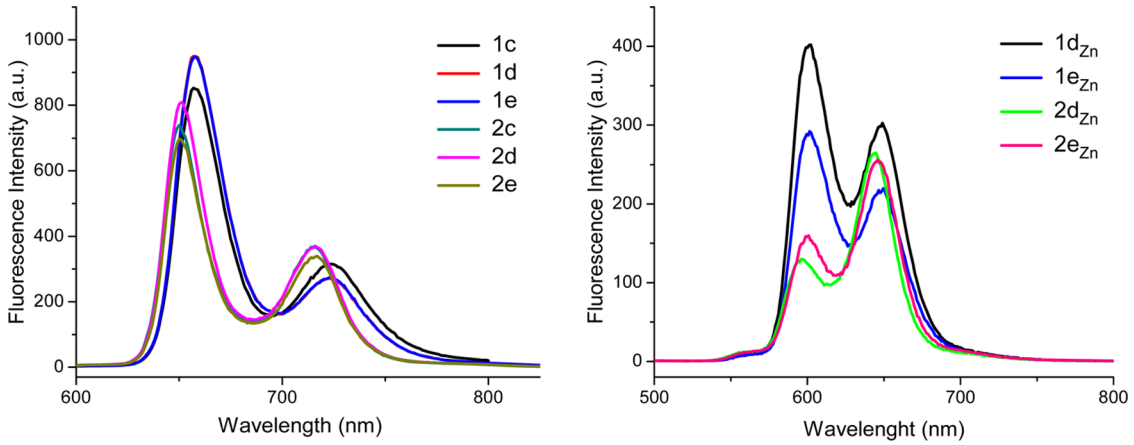

Figure 4. Emission spectra of starting porphyrin-cored dendrimers in $CHCl_3$ (λ_{ex} = 422 nm): free-base dendrimers (left); metalated dendrimers (right).

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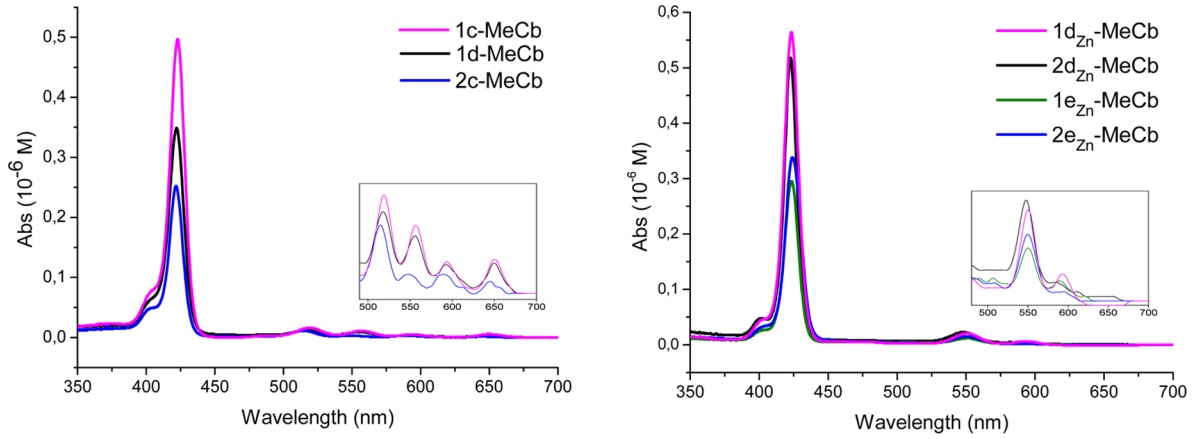

Figure 5. UV−vis spectra in $CHCl_3$ of carboranyl-containing dendrimers: free-base dendrimers (left); metalated dendrimers (right).

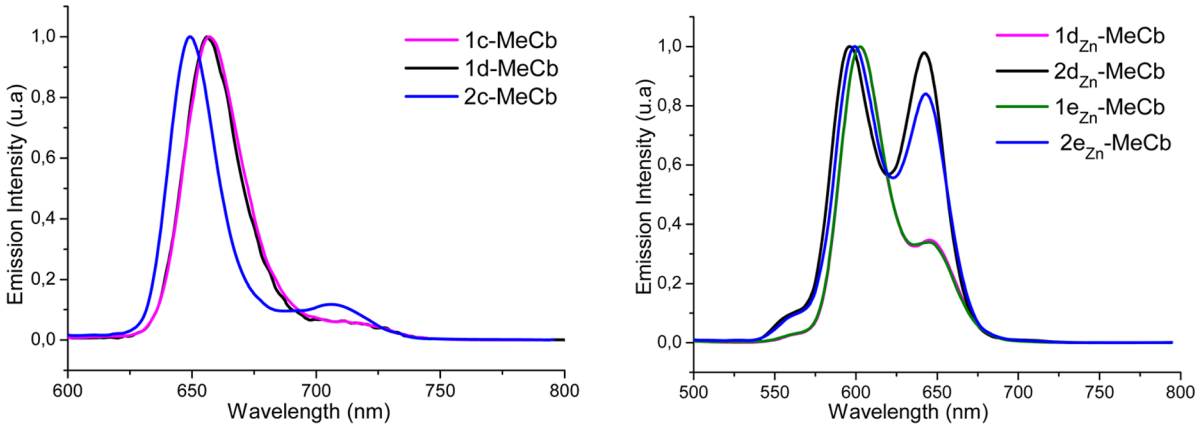

Figure 6. Emission spectra of carboranyl-containing dendrimers in $CHCl_3$ (λ_{ex} = 422 nm): free-base dendrimers (left); metalated dendrimers (right).

that can be important to benefitting from the individual property of the porphyrin and carborane clusters.

EXPERIMENTAL SECTION

Instrumentation. IR spectra were measured on PerkinElmer Spectrum 400 FT-IR/FT-FIR and Shimadzu FTIR-ATR-8300 spectrophotometers (units are reciprocal centimeters). ^{1}H NMR (300.13 and 400 MHz) and $^{13}C\{^1H\}$ (75.47 and 100.5 MHz) spectra were recorded using Varian Unity Inova 400 MHz and Bruker ARX 300 spectrometers. The ^{11}B NMR (96.29 MHz) spectra were recorded on a Bruker ARX 300 spectrometer. All experiments were done with concentrations between 15 and 20 mg/mL at 25 °C. Chemical shifts (ppm) are relative to $Si(CH_3)_4$ for ^{1}H (of residual proton; 7.25 ppm) and ^{13}C (77.23 ppm) in $CDCl_3$. Chemical shift values for ^{11}B NMR spectra were referenced to external $BF_3{\cdot}OEt_2$. Chemical shifts are reported in units of parts per million downfield from the reference, and all coupling constants are reported in Hertz. Mass spectra were obtained from a Thermo-Electron DFS spectrometer instrument by an electron impact (EI) ionization technique, and the AB SCIEX 4800 Plus MALDI TOF/TOF analyzer has the highest sensitivity available in MS and MS/MS mode. UV−vis spectra were recorded on PerkinElmer Lambda 900 and Shimadzu UV-1700 Pharmaspec spectrophotometers using 1.0 cm cuvettes. The fluorescence emission spectra of the starting dendrimers were recorded on a Varian Cary Eclipse fluorescence spectrometer. The fluorescence emission spectra of the carboranyl-containing dendrimers were recorded on a PerkinElmer LS-45 (230 V) fluorescence spectrometer. Samples were prepared in spectroscopic-grade solvents and adjusted to a response within the linear range. No fluorescent contaminants were detected upon excitation in the wavelength region of experimental interest. Elemental analyses were performed using a Carlo Erba EA1108 microanalyzer.

Materials. All reactions were performed under an atmosphere of dinitrogen employing standard Schlenk techniques. The solvents were reagent grade and were purified by distillation from the appropriate drying agents before use. The pyrrole, *p*-$CH_3OC_6H_4CHO$, 3,5-$(CH_3O)_2C_6H_4CHO$, CH_3CH_2COOH, 48% HBr, allyl bromide, $LiAlH_4$, $SOCl_2$, C_5H_5N, and K_2CO_3 were provided by Sigma-Aldrich, glacial CH_3COOH was provided by J. T. Baker, and 1-CH_3-1,2-*closo*-$C_2B_{10}H_{11}$ was supplied by Katchem Ltd. (Prague) and used as received. Karstedt's catalyst (9.21% Pt) was purchased from Johnson Matthey. The *n*-BuLi solution (1.6 M in hexanes) and 1-(CH_3)-2-$[CH_2CH_2CH_2Si(CH_3)_2H]$-1,2-*closo*-$C_2B_{10}H_{10}$ were prepared according to the literature.[12] Compounds **1a**,[43] **2a**,[44] **1b**,[48] **2b**,[49] **Br-dendron-1**,[50−53] and **Br-dendron-2**,[54,55] were prepared following literature processes; in some specific cases, little modification was done (see the SI). UV−vis spectroscopic data for all of these are in agreement with the data reported in the literature.

Procedure for the Preparation of Dendrimers 1c−1e and 2c−2e. A round-bottomed flask equipped with a condenser and a magnetic stirring bar was charged with porphyrin **1b** or **2b**, allyl bromide, or **Br-dendron-1** or **Br-dendron-2**, with K_2CO_3 and a catalytic amount of KI, using acetone as the solvent. The mixture was refluxed for 16 h, monitoring the reaction by TLC. After that, the reaction mixture was filtered and the volatiles were evaporated under vacuum. The solid product was washed with hexane and methanol to remove impurities to obtain dendrimers **1c** with 4, **1d** and **2c** with 8, **1e** and **2d** with 16, and finally **2e** with 32 allyl groups present in the periphery of the dendrimers.

*meso-Tetrakis(4-allyloxyphenyl)porphyrin (**1c**).* The title compound was prepared with **1b** (1.00 g, 1.50 mmol), allyl bromide (1.43 g, 11.70 mmol), K_2CO_3 (2.44 g), and a catalytic amount of KI in

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acetone. Compound **1c** was obtained as a purple solid (1.07 g, 87% yield). Mp: 250−252 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.85 (s, 8H, H-β), 8.09 (d, 8H, J = 8.5 Hz, H-2), 7.26 (d, 8H, J = 8.5 Hz, H-3), 6.25 (ddt, 4H, J = 16.5, 10.5, and 5.1 Hz, H-6), 5.59 (dd, 4H, J = 16.5 and 1.2 Hz, H-7a), 5.43 (dd, 4H, J = 10.5 and 1.5 Hz, H-7b), 4.78 (d, 8H, J = 5.1 Hz, H-5), −2.75 (s, 2H, NH). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 158.6 (C-4), 135.8 (C-2), 135.0 (C-1), 133.6 (C-6), 131.2 (C-β), 119.9 (*meso*-C), 118.2 (C-7), 113.2 (C-3), 69.3 (C-5). IR (KBr): ν 3319 (N−H), 1605 (C═C), 1506, 1241 (C−O), 1224, 1175, 803 (C−H), 739 cm^{-1}. MS [m/z (%)]: [M$^+$ + H] 839 (25), 838 (19), 391 (12), 307 (15), 192 (25), 154 (100), 136 (70), 95 (74), 69 (94). UV−vis ($CHCl_3$): λ_{max} = 422 nm (ε = 342680 M^{-1} cm^{-1}).

*meso-Tetrakis(3,5-diallyloxyphenyl)porphyrin (**2c**).* The title compound was prepared from **2b** (1.00 g, 1.35 mmol), allyl bromide (1.30 g, 10.7 mmol), K_2CO_3 (3.20 g, 23.2 mmol), and KI in acetone. Compound **2c** was obtained as a purple solid, (1.20 g, 84% yield). Mp: 205−207 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.93 (s, 8H, H-β), 7.42 (d, 8H, J = 2.4 Hz, H-2), 6.95 (t, 4H, J = 2.4 Hz), 6.14 (ddt, 8H, J = 17.2, 10.5, and 5.3 Hz, H-6), 5.49 (ddt, 8H, J = 17.2, 1.6, and 1.2 Hz, H-7a), 5.33 (ddt, 8H, J = 10.5, 1.5, and 1.2 Hz, H-7b), 4.71 (dt, 16H, J = 5.3 and 1.2 Hz, H-5), −2.85 (s, 2H, NH). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 158.0 (C-3), 144.2 (C-1), 133.4 (C-6), 131.3 (C-β), 120.0 (*meso*-C), 118.2 (C-7), 115.0 (C-2), 101.8 (C-4), 69.4 (C-5). IR (KBr): ν 3317 (N−H), 1588 (C═C), 1506, 1290 (C−O) cm^{-1}. MS [m/z (%)]: [M$^+$ + H] 1063. UV−vis ($CHCl_3$): λ_{max} = 422 nm (ε = 380165 M^{-1} cm^{-1}).

*meso-Tetrakis[4-[3,5-bis(allyloxy)benzyloxy]phenyl]porphyrin (**1d**).* The title compound was obtained from **1b** (0.50 g, 0.74 mmol), **Br-dendron-1** (0.70 g, 2.95 mmol), K_2CO_3 (1.22 g, 8.84 mmol), and KI in acetone. The solid compound was purified by column chromatography using a mixture of hexane/acetone (8:2). The product **1d** was obtained as a purple solid (0.84 g, 77% yield). Mp: 140−144 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.86 (s, 8H, H-β), 8.12 (d, 8H, J = 8.6 Hz, H-2), 7.34 (d, 8H, J = 8.6 Hz, H-3), 6.80 (d, 8H, J = 2.2 Hz, H-7), 6.55 (t, 4H, J = 2.2 Hz, H-9), 6.11 (ddt, 8H, J = 17.3, 10.5, and 5.3 Hz, H-11), 5.47 (ddt, 8H, J = 17.3, 1.6, and 1.6 Hz, H-12a), 5.34 (ddt, 8H, J = 10.5, 1.4, and 1.6 Hz, H-12b), 5.27 (s, 8H, H-5), 4.62 (dt, 16H, J = 5.3 and 1.2 Hz, H-10), −2.76 (s, 2H, NH). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 160.3 (C-8), 158.8 (C-4), 139.6 (C-6), 135.8 (C-2), 135.2 (C-1), 133.4 (C-11), 131.2 (C-β), 119.9 (*meso*-C), 118.1 (C-12), 113.3 (C-3), 106.6 (C-7), 101.7 (C-9), 70.5 (C-5), 69.2 (C-10). IR (KBr): ν 3316 (N−H), 1597 (C═C), 1506, 1455, 1240, 1171, 1019 (C−O), 802 (C−H), 735 cm^{-1}. MS [m/z (%)]: [M$^+$ + H] 1487 (68), 1486 (40), 1285 (20), 203 (74), 154 (100), 136 (80), 121 (70), 69 (58). UV−vis ($CHCl_3$): λ_{max} = 423 nm (ε = 343425 M^{-1} cm^{-1}).

*meso-Tetrakis[3,5-[3,5-bis(allyloxy)dibenzyloxy]phenyl]porphyrin (**2d**).* The title compound was obtained from **2b** (0.50 g, 0.74 mmol), **Br-dendron-1** (1.30 g, 5.4 mmol), K_2CO_3 (2.20 g, 16.2 mmol), and KI in acetone. The solid was purified by column chromatography using a mixture of hexane/acetone (8:2). The product **2d** was obtained as a purple oil (0.84 g, 60% yield). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.88 (s, 8H, H-β), 7.49 (d, 8H, J = 2.2 Hz, H-2), 7.05 (t, 4H, J = 2.2 Hz, H-4), 6.67 (d, 16H, J = 2.3 Hz, H-7), 6.47 (t, 8H, J = 2.3 Hz, H-9), 5.99 (ddt, 16H, J = 17.3, 10.5, and 5.3 Hz, H-11), 5.35 (ddt, 16H, J = 17.3, 1.6, and 1.6 Hz, H-12a), 5.21 (ddt, 16H, J = 10.5, 1.6, and 1.4 Hz, H-12b), 5.16 (s, 16H, H-5), 4.49 (dt, 32H, J = 5.3 and 1.4 Hz, H-10), −2.87 (s, 2H, NH). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 160.2 (C-8), 158.1 (C-3), 144.2 (C-1), 139.3 (C-6), 133.3 (C-11), 119.9 (*meso*-C), 118.0 (C-12), 115.4 (C-2), 106.5 (C-7), 101.8 (C-4, C-9), 70.5 (C-5), 69.1 (C-10). IR (KBr): ν 3317 (N−H), 1597 (C═C), 1506, 1455, 1295, 1171, 1019 (C−O) cm^{-1}. MS [m/z (%)]: [M$^+$] 2360. UV−vis ($CHCl_3$): λ_{max} = 423 nm (ε = 240225 M^{-1} cm^{-1}).

*meso-Tetrakis[4-[3,5-bis(3,5-bis(allyloxy)benzyloxy)benzyloxy]-phenyl]porphyrin (**1e**).* The title compound was obtained from **1b** (0.5 g, 0.74 mmol), **Br-dendron-2** (0.86 g, 1.54 mmol), and K_2CO_3 (0.46 g, 3.33 mmol) in the presence of KI in acetone. The solid obtained was purified by column chromatography using a mixture of hexane/acetone (8:2). The product **1e** was obtained as a red solid (0.52 g, 49% yield). Mp: 53−57 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.87 (s, 8H, H-β), 8.13 (d, 8H, J = 8.5 Hz, H-2), 7.35 (d, 8H, J = 8.5 Hz, H-3), 6.88 (d, 8H, J = 2.2 Hz, H-7), 6.66 (d, 16H, J = 2.3 Hz, H-12), 6.64 (t, 4H, J = 2.2 Hz, H-9), 6.48 (t, 8H, J = 2.3 Hz, H-14), 6.05 (ddt, 16H, J = 17.3, 10.5, and 5.3 Hz, H-16), 5.41 (ddt, 16H, J = 17.3, 1.6, and 1.5 Hz, H-17a), 5.27 (ddt, 16H, J = 10.5, 1.5, and 1.4 Hz, H-17b), 5.28 (s, 8H, H-5), 5.06 (s, 16H, H-10), 4.54 (dt, 32H, J = 5.3 and 1.5 Hz, H-15), −2.78 (s, 2H, NH). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 160.4 (C-8), 160.2 (C-13), 158.8 (C-4), 139.7 (C-6), 139.4 (C-11), 135.9 (C-2), 135.2 (C-1), 133.3 (C-16), 133.2 (C-β), 119.9 (*meso*-C), 118.0 (C-17), 113.3 (C-3), 106.9 (C-7), 106.5 (C-12), 102.0 (C-9), 101.6 (C-14), 70.5 (C-5), 70.4 (C-10), 69.2 (C-15). IR (KBr): ν 3316 (N−H), 1596 (C═C), 1507, 1450, 1240, 1150, 1046 (C−O), 831 (C−H), 802, 731 cm^{-1}. MS (MALDI): m/z 2785. UV−vis ($CHCl_3$): λ_{max} = 423 nm (ε = 362830 M^{-1} cm^{-1}).

*meso-Tetrakis[3,5-[3,5-bis(3,5-bis(allyloxy)benzyloxy)-dibenzyloxy]phenyl]porphyrin (**2e**).* The title compound was obtained from **2b** (0.18 g, 0.24 mmol), **Br-dendron-2** (1.10 g, 1.90 mmol), and K_2CO_3 (81.00 g, 5.8 mmol) in the presence of KI in acetone. The solid obtained was purified by column chromatography using a mixture of hexane/acetone (8:2). Compound **2e** was obtained as a deep-purple oil (0.52 g, 58% yield). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.91 (s, 8H, H-β), 7.49 (s, 8H, H-2), 7.05 (s, 4H, H-4), 6.73 (s, 16H, H-7), 6.54 (s, 8H, H-9), 6.51 (s, 32H, H-12), 6.37 (s, 16H, H-14), 5.93 (ddt, 32H, J = 17.3, 10.5, and 5.2 Hz, H-16), 5.29 (dt, 32H, J = 17.3 and 1.3 Hz, H-17a), 5.17 (dt, 32H, J = 10.5 and 1.1 Hz, H-17b), 5.12 (s, 16H, H-5), 4.91 (s, 32H, H-10), 4.40 (d, 64H, J = 5.2 Hz, H-15), −2.83 (s, 2H, NH). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 160.3 (C-8), 160.1 (C-13), 158.2 (C-3), 139.3 (C-11), 136.8 (C-6), 133.3 (C-16), 117.9 (C-17), 115.3 (C-2), 106.9 (C-7), 106.3 (C-12), 102.1 (C-4, C-9), 101.6 (C-14), 70.5 (C-5), 70.2 (C-10), 69.0 (C-15). IR (KBr): ν 3317 (N−H), 1594 (C═C), 1507, 1450, 1296, 1150, 1046 (C−O) cm^{-1}. UV−vis ($CHCl_3$): λ_{max} = 423 nm (ε = 268265 M^{-1} cm^{-1}).

Procedure for the Metalation of Compounds 1d, 1e, 2d, and 2e. Metalation of the porphyrin was carried out using conditions reported previously.[46] A round-bottomed flask equipped with a condenser and a magnetic stirring bar was charged with **1d** (or **1e**, **2d**, or **2e**) and $Zn(CH_3COO)_2{\cdot}2H_2O$ (the same amount in grams as the porphyrin) in 70 mL of DMF, and the mixture was refluxed for 30 min. After cooling to room temperature, the solid was precipitated by the addition of cold water and washed with methanol to remove traces of DMF.

*[meso-Tetrakis[4-[3,5-bis(allyloxy)benzyloxy]phenyl]-porphyrinato]zinc(II) (**1d$_{Zn}$**).* The title compound was obtained from **1b** (0.70 g, 0.47 mmol) and $Zn(CH_3COO)_2{\cdot}2H_2O$ (0.70 g, 3.19 mmol). Compound **1d$_{Zn}$** was obtained as a purple solid (0.61 g, 83% yield). Mp: 139−141 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.97 (s, 8H, H-β), 8.12 (d, 8H, J = 8.3 Hz, H-2), 7.33 (d, 8H, J = 8.3 Hz, H-3), 6.78 (s, 8H, H-7), 6.52 (s, 4H, H-9), 6.10 (ddt, 8H, J = 17.3, 10.5, and 5.3 Hz, H-11), 5.46 (d, 8H, J = 17.3 Hz, H-12a), 5.33 (d, 8H, J = 10.5 Hz, H-12b), 5.26 (s, 8H, H-5), 4.59 (d, 16H, J = 5.3 Hz, H-10). ^{13}C NMR ($CDCl_3$, 100.5 MHz): δ 160.3 (C-8), 158.6 (C-4), 150.7 (C-α), 139.7 (C-6), 135.8 (C-1), 135.7 (C-2), 133.4 (C-11), 132.1 (C-β), 120.9 (*meso*-C), 118.1 (C-12), 113.2 (C-3), 106.6 (C-7), 101.7 (C-9), 70.5 (C-5), 69.2 (C-10). IR (KBr): ν 1595 (C═C), 1506, 1453, 1220, 1161, 1148, (C−H), 994, 796 cm^{-1}. UV−vis ($CHCl_3$): λ_{max} = 423 nm (ε = 430265 M^{-1} cm^{-1}).

*[meso-Tetrakis[3,5-[3,5-bis(allyloxy)dibenzyloxy]phenyl]-porphyrinato]zinc(II) (**2d$_{Zn}$**).* The title compound was obtained from **2d** (0.60 g, 0.25 mmol) and $Zn(CH_3COO)_2{\cdot}2H_2O$ (0.60 g, 2.73 mmol). Compound **2d$_{Zn}$** was obtained as a purple solid (0.52 g, 85% yield). Mp: 65−67 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.99 (s, 8H, H-β), 7.49 (s, 8H, H-2), 7.03 (s, 4H, H-4), 6.66 (s, 16H, H-7), 6.45 (s, 8H, H-9), 5.99 (ddt, 16H, J = 17.2, 10.0, and 5.2 Hz, H-11), 5.34 (d, 16H, J = 17.2 Hz, H-12a), 5.21 (d, 16H, J = 10.0 Hz, H-12b), 5.14 (s, 16H, H-5), 4.49 (d, 32H, J = 5.2 Hz, H-10). ^{13}C NMR ($CDCl_3$, 100.5 MHz): δ 160.2 (C-8), 158.0 (C-3),150.2 (C-α) 144.9 (C-1), 139.4 (C-6), 133.3 (C-11), 132.2 (C-β), 120.9 (*meso*-C), 118.0 (C-12), 115.3 (C-2), 106.5 (C-7), 102.2 (C-4), 101.7 (C-9), 70.5 (C-5), 69.1 (C-10). IR (KBr): ν 1587 (C═C), 1449, 1294, 1145, 1049 (C−O), 1000, 923 cm^{-1}. UV−vis ($CHCl_3$): λ_{max} = 424 nm (ε = 303005 M^{-1} cm^{-1}).

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*[meso-Tetrakis[4-[3,5-bis[3,5-bis(allyloxy)benzyloxy]benzyloxy]-phenyl]porphyrinato]zinc(II) (**1e**$_{Zn}$).* The title compound was obtained from **1e** (0.50 g, 0.22 mmol) and $Zn(CH_3COO)_2{\cdot}2H_2O$ (0.50 g, 2.73 mmol). Compound **1e**$_{Zn}$ was obtained as a purple solid (0.52 g, 85% yield). Mp: 76−78 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.98 (s, 8H, H-β), 8.13 (d, 8H, J = 7.9 Hz, H-2), 7.33 (d, 8H, J = 7.9 Hz, H-3), 6.82 (s, 8H, H-7), 6.60 (s, 16H, H-12), 6.58 (s, 4H, H-9), 6.43 (s, 8H, H-14), 6.02 (ddt, 16H, J = 17.3, 10.5, and 3.4 Hz, H-16), 5.39 (d, 16H, J = 17.3 Hz, H-17a), 5.26 (d, 16H, J = 10.5 Hz, H-17b), 5.22 (s, 16H, H-5), 4.99 (s, 16H, H-10), 4.50 (d, 32H, J = 3.4 Hz, H-15). ^{13}C NMR ($CDCl_3$, 100.5 MHz): δ 160.3 (C-8), 160.1 (C-13), 158.6 (C-4), 150.6 (C-α), 139.6 (C-6), 139.3 (C-11), 135.9 (C-1), 135.7 (C-2), 133.3 (C-16), 132.1 (C-β), 120.8 (*meso*-C), 117.9 (C-17), 113.1 (C-3), 106.9 (C-7), 106.4 (C-12), 102.0 (C-9), 101.6 (C-14), 70.4 (C-5), 70.2 (C-10), 69.1 (C-15). IR (KBr): ν 1592 (C═C), 1447, 1242, 1144, 1042 (C−O), 993, 829 cm^{-1}. UV−vis ($CHCl_3$): λ_{max} = 423 nm (ε = 260520 M^{-1} cm^{-1}).

*[meso-Tetrakis[3,5-[3,5-bis[3,5-bis(allyloxy)benzyloxy]-dibenzyloxy]phenyl]porphyrinato]zinc(II) (**2e**$_{Zn}$).* The title compound was obtained from **2e** (0.48 g, 0.1 mmol) and $Zn(CH_3COO)_2{\cdot}2H_2O$ (0.48 g, 2.19 mmol). Compound **2e**$_{Zn}$ was obtained as a purple solid (0.390 g, 80% yield). Mp: 59−61 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.01 (s, 8H, H-β), 7.50 (d, 8H, J = 2.3 Hz, H-2), 7.05 (t, 4H, J = 2.3 Hz, H-4), 6.73 (d, 16H, J = 2.1 Hz, H-7), 6.54 (t, 8H, J = 2.1 Hz, H-9), 6.49 (d, 32H, J = 2.2 Hz, H-12), 6.34 (t, 16H, J = 2.2 Hz, H-14), 5.91 (ddt, 32H, J = 17.2, 10.5, and 5.3 Hz, H-16), 5.28 (dt, 32H, J = 17.2 and 1.6 Hz, H-17a), 5.16 (dt, 32H, J = 10.5 and 1.3 Hz, H-17b), 5.12 (s, 16H, H-5), 4.91 (s, 32H, H-10), 4.38 (dt, 64H, J = 5.3 and 1.4 Hz, H-15). ^{13}C NMR ($CDCl_3$, 100.5 MHz): δ 160.3 (C-8), 160.0 (C-13), 158.0 (C-3), 150.1 (C-α), 144.9 (C-1), 139.4 (C-6), 139.2 (C-11), 133.2 (C-16), 132.2 (C-β), 120.8 (*meso*-C), 117.8 (C-17), 115.2 (C-2), 106.8 (C-7), 106.3 (C-12), 101.9 (C-4 and C-9), 101.5 (C-14), 70.5 (C-5), 70.2 (C-10), 69.0 (C-15). IR (KBr): ν 1591 (C═C), 1447, 1295, 1146, 1047 (C−O), 1046, 1001, 830 cm^{-1}. UV−vis ($CHCl_3$): λ_{max} = 425 nm (ε = 331535 M^{-1} cm^{-1}).

1c-MeCb. A 5 mL round-bottomed flask was charged with **1c** (60 mg, 0.072 mmol) and 1-CH_3-2-$[CH_2CH_2CH_2(CH_3)_2SiH]$-1,2-*closo*-$C_2B_{10}H_{10}$ (111 mg, 0.430 mmol) and dried under vacuum for 15 min. The mixture was dissolved in 1 mL of dry CH_2Cl_2, and 12 μL of Karstedt's catalyst was added and refluxed for 5 h under nitrogen. The volatiles were removed under pressure to obtain a brown-purple oil, which was purified by preparative TLC (1:1 dichloromethane/hexane) and precipitated with 1:1 dichloromethane/ethanol, giving a purple solid (95 mg, 71% yield). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.91 (s, 8H, H-β), 8.16 (d, 8H, ^3J(H,H) = 9 Hz, H-2), 7.30 (d, 8H, ^3J(H,H) = 12 Hz, H-3), 4.24 (t, 16H, ^3J = 6 Hz, H-5), 2.26 (t, 16H, ^3J = 9 Hz, H-11), 2.05 (s, 24H, H-14), 1.99 (m, 16H, H-6), 1.67 (m, 16H, H-10), 0.84 (t, 16H, ^3J = 9 Hz, H-7), 0.66 (t, 16H, ^3J = 9 Hz, H-9), 0.16 (s, 48H, H-8), −2.69 (br s, 2H, NH). ^{11}B NMR ($CDCl_3$, 96.7 MHz): δ −5.86 (d, 8B, $^1J_{B,H}$ = 147 Hz), −10.79 (d, 32B, $^1J_{B,H}$ = 142 Hz). ^{13}C{^{1}H} NMR ($CDCl_3$, 75.5 MHz): δ 158.91 (C-4), 135.66 (C-2), 134.47 (C-1), 131.07 (C-β), 119.80 (*meso*-C), 112.76 (C-3), 78.11 (C-12), 74.66 (C-13), 70.72 (C-5), 39.04 (C-11), 24.30 (C-10), 24.00 (C-6), 23.19 (C-14), 15.29 (C-7), 11.32 (C-9), −3.42 (C-8). FTIR-ATR: ν 2579 (i, B−H str) cm^{-1}. Elem anal. Calcd for $C_{88}H_{150}B_{40}N_4O_4Si_4$: C, 56.43; H, 8.07; N, 2.99. Found: C, 56.82; H, 8.40; N, 2.90.

1d-MeCb. The title compound was obtained from **1d** (30 mg, 0.020 mmol), 1-CH_3-2-$[CH_2CH_2CH_2(CH_3)_2SiH]$-1,2-*closo*-$C_2B_{10}H_{10}$ (63 mg, 0.244 mmol), and 10 μL of Karstedt's catalyst in 1 mL of $CHCl_3$ stirred at 50 °C for 5 h. The reaction mixture was purified by preparative TLC (acetonitrile) and precipitated with 1:1 ether/ethanol, giving a purple solid (46 mg, 64% yield). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.92 (s, 8H, H-β), 8.18 (d, 8H, ^3J = 6 Hz, H-2), 7.41 (d, 8H, ^3J = 6 Hz, H-3), 6.82 (s, 8H, H-7), 6.54 (s, 4H, H-9), 5.32 (s, 8H, H-5), 4.05 (t, 16H, ^3J = 6 Hz, H-10), 2.21 (t, 16H, ^3J = 7.5 Hz, H-16), 2.02 (s, 24H, H-19), 1.87 (m, 16H, H-11), 1.61 (m, 16H, H-15), 0.73 (t, 16H, ^3J = 9 Hz, H-12), 0.60 (t, 16H, ^3J = 9 Hz, H-14), 0.10 (s, 48H, H-13), −2.70 (br s, 2H, NH). ^{11}B NMR ($CDCl_3$, 96.7 MHz): δ −5.91 (d, 16B, $^1J_{B,H}$ = 148 Hz), −10.78 (d, 64B, $^1J_{B,H}$ = 140 Hz). ^{13}C{^{1}H} NMR ($CDCl_3$, 75.5 MHz): δ 160.6 (C-8), 158.7 (C-4), 139.4 (C-6), 135.7 (C-2), 135.0 (C-1), 131.2 (C-β), 119.7 (*meso*-C), 113.2 (C-3), 106.0 (C-7), 101.0 (C-9), 78.1 (C-17), 74.6 (C-18), 70.7 (C-10), 70.5 (C-5), 39.0 (C-16), 24.3 (C-15), 23.9 (C-11), 23.1 (C-19), 15.3 (C-12), 11.2 (C-14), −3.4 (C-13). FTIR-ATR: ν 2578 (i, B−H str) cm^{-1}. Elem anal. Calcd for $C_{160}H_{294}B_{80}N_4O_{12}Si_8$: C, 54.05; H, 8.33; N, 1.58. Found: C, 54.00; H, 8.00; N, 1.55.

2c-MeCb. The title compound was obtained from **2c** (60 mg, 0.056 mmol), 1-CH_3-2-$[CH_2CH_2CH_2(CH_3)_2SiH]$-1,2-*closo*-$C_2B_{10}H_{10}$ (231 mg, 0.896 mmol), and 15 μL of Karstedt's catalyst in 1 mL of $CHCl_3$ stirred at 50 °C for 5 h. The reaction mixture was purified by preparative TLC (1:1 dichloromethane/hexane) and precipitated with 1:1 dichloromethane/ethanol, giving a purple solid (127 mg, 72% yield). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.96 (s, 8H, H-β), 7.38 (s, 8H, H-2), 6.91 (s, 4H, H-4), 4.11 (t, 16H, ^3J = 6 Hz, H-7), 2.14 (t, 16H, ^3J = 7.5 Hz, H-13), 1.91 (s, 24H, H-16), 1.87 (m, 16H, H-8), 1.54 (m, 16H, H-12), 0.69 (t, 16H, ^3J = 7.5 Hz, H-9), 0.55 (t, 16H, ^3J = 7.5 Hz, H-11), 0.05 (s, 64H, H-10), −2.82 (br s, 2H, NH). ^{11}B NMR ($CDCl_3$, 96.7 MHz): δ −5.87 (d, 16B, $^1J_{B,H}$ = 145 Hz), −10.77 (d, 64B, $^1J_{B,H}$ = 138 Hz). ^{13}C{^{1}H} NMR ($CDCl_3$, 75.5 MHz): δ 158.3 (C-3), 143.9 (C-1), 131.2 (C-β), 119.9 (*meso*-C), 114.4 (C-2), 101.1 (C-4), 78.1 (C-14), 74.6 (C-15), 70.8 (C-7), 38.9 (C-13), 24.3 (C-12), 23.9 (C-8), 23.1 (C-16), 15.2 (C-9), 11.2 (C-11), −3.5 (C-10). FTIR-ATR: ν 2578 (i, B−H str) cm^{-1}. Elem anal. Calcd for $C_{132}H_{270}B_{80}N_4O_8Si_8$: C, 50.63; H, 8.69; N, 1.79. Found: C, 51.60; H, 9.04; N, 1.65.

1d$_{Zn}$-MeCb. The title compound was obtained from **1d**$_{Zn}$ (31 mg, 0.020 mmol), 1-CH_3-2-$[CH_2CH_2CH_2(CH_3)_2SiH]$-1,2-*closo*-$C_2B_{10}H_{10}$ (62 mg, 0.240 mmol), and 15 μL of Karstedt's catalyst in 1 mL of $CHCl_3$ stirred at 50 °C for 5 h. The reaction mixture was purified by preparative TLC (acetonitrile) and precipitated with 1:1 dichloromethane/ethanol, giving a purple solid (59 mg, 82% yield). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 9.01 (s, 8H, H-β), 8.17 (d, 8H, ^3J = 9 Hz, H-2), 7.39 (d, 8H, ^3J = 6 Hz, H-3), 6.80 (s, 8H, H-7), 6.51 (s, 4H, H-9), 5.31 (s, 8H, H-5), 4.03 (t, ^3J = 6 Hz, 16H, H-10), 2.20 (t, ^3J = 7.5 Hz, 16H, H-16), 2.02 (s, 24H, H-19), 1.86 (m, 16H, H-11), 1.60 (m, 16H, H-15), 0.72 (t, 16H, ^3J = 9 Hz, H-12), 0.59 (t, 16H, ^3J = 9 Hz, H-14), 0.09 (s, 48H, H-13). ^{11}B NMR ($CDCl_3$, 96.7 MHz): δ −5.88 (d, 16B, $^1J_{B,H}$ = 146 Hz), −10.75 (d, 64B, $^1J_{B,H}$ = 139 Hz). ^{13}C{^{1}H} NMR ($CDCl_3$, 75.5 MHz): δ 160.6 (C-8), 158.6 (C-4), 150.5 (C-α), 140.4 (C-1), 139.4 (C-6), 135.5 (C-2), 131.9 (C-β), 120.8 (*meso*-C), 106.0 (C-7), 101.1 (C-9), 78.1 (C-17), 74.6 (C-18), 70.7 (C-5), 70.7 (C-10), 39.0 (C-16), 24.3 (C-15), 23.9 (C-11), 23.1 (C-19), 15.3 (C-14), 11.2 (C-12), −3.4 (C-13). FTIR-ATR: ν 2578 (i, B−H str) cm^{-1}. Elem anal. Calcd for $C_{160}H_{292}B_{80}N_4O_{12}Si_8Zn$: C, 53.10; H, 8.13; N, 1.55. Found: C, 53.38; H, 8.18; N, 1.45.

2d$_{Zn}$-MeCb. The title compound was obtained from **2d**$_{Zn}$ (40 mg, 0.0165 mmol), 1-CH_3-2-$[CH_2CH_2CH_2(CH_3)_2SiH]$-1,2-*closo*-$C_2B_{10}H_{10}$ (137 mg, 0.531 mmol), and 15 μL of Karstedt's catalyst in 1 mL of 1,4-dioxane stirred at 55 °C for 5 h. The reaction mixture was purified by preparative TLC (70:30 acetonitrile/ethyl acetate) and precipitated with 1:1 dichloromethane/ethanol, giving a purple solid (95 mg, 88% yield). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 9.09 (s, 8H, H-β), 7.56 (s, 8H, H-2), 7.10 (s, 4H, H-4), 6.67 (s, 16H, H-7), 6.44 (s, 8H, H-9), 5.16 (s, 16H, H-5), 3.93 (br s, 32H, H-10), 2.13 (t, 32H, ^3J = 7.5 Hz, H-16), 1.95 (s, 48H, H-19), 1.77 (m, 16H, H-11), 1.53 (m, 16H, H-15), 0.62 (br s, 16H, H-12), 0.51 (br s, 16H, H-14), 0.01 (s, 96H, H-13). ^{11}B NMR ($CDCl_3$, 96.7 MHz): δ −5.94 (d, 32B, $^1J_{B,H}$ = 153 Hz), −10.70 (d, 128B, $^1J_{B,H}$ = 130 Hz). ^{13}C{^{1}H} NMR ($CDCl_3$, 75.5 MHz): δ 160.5 (C-8), 158.1 (C-3), 150.1 (C-α), 144.7 (C-1), 1389.0 (C-6), 132.0 (C-β), 120.8 (*meso*-C), 114.9 (C-2), 106.0 (C-7), 101.5 (C-4), 101.0 (C-9), 78.1 (C-17), 74.6 (C-18), 70.6 (C-5), 70.6 (C-10), 38.9 (C-16), 24.2 (C-15), 23.8 (C-11), 23.1 (C-19), 15.2 (C-12), 11.1 (C-14), −3.5 (C-13). FTIR-ATR: ν 2578 (i, B−H str) cm^{-1}. Elem anal. Calcd for $C_{276}H_{556}B_{160}N_4O_{24}Si_{16}Zn$: C, 50.53; H, 8.54; N, 0.85. Found: C, 51.03; H, 8.67; N, 0.78.

1e$_{Zn}$-MeCb. The title compound was obtained from **1e**$_{Zn}$ (25 mg, 0.0088 mmol), 1-CH_3-2-$[CH_2CH_2CH_2(CH_3)_2SiH]$-1,2-*closo*-$C_2B_{10}H_{10}$ (72 mg, 0.279 mmol), and 20 μL of Karstedt's catalyst in 1 mL of 1,4-dioxane stirred at 60 °C for 5 h. The reaction mixture was purified by preparative TLC (acetonitrile) and precipitated with 1:1 dichloromethane/ethanol, giving a purple solid (42 mg, 69% yield). ^{1}H

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NMR ($CDCl_3$, 300 MHz): δ 9.05 (s, 8H, H-β), 8.21 (d, 8H, ^3J = 9 Hz, H-2), 7.43 (d, 8H, ^3J = 6 Hz, H-3), 6.96 (s, 8H, H-7), 6.71 (s, 4H, H-9), 6.67 (s, 16H, H-12), 6.47 (s, 8H, H-14), 5.34 (s, 8H, H-5), 5.11 (s, 16H, H-10), 3.98 (t, 32H, ^3J = 6 Hz, H-15), 2.18 (t, 32H, ^3J = 9 Hz, H-21), 2.00 (s, 48H, H-24), 1.82 (m, 32H, H-16), 1.58 (m, 32H, H-20), 0.69 (t, 32H, ^3J = 9 Hz, H-17), 0.56 (t, 32H, ^3J = 9 Hz, H-19), 0.07 (s, 96H, H-18). ^{11}B NMR ($CDCl_3$, 96.7 MHz): δ −5.89 (d, 32B, $^1J_{B,H}$ = 148 Hz), −10.77 (d, 128B, $^1J_{B,H}$ = 140 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.5 MHz): δ 160.5 (C-13), 160.4 (C-8), 158.6 (C-4), 150.5 (C-α), 139.6 (C-6), 139.1 (C-11), 135.7 (C-1), 135.5 (C-2), 1312.0 (C-β), 120.8 (*meso*-C), 113.0 (C-3), 106.7 (C-7), 106.0 (C-12), 101.8 (C-9), 101.0 (C-14), 78.2 (C-22), 74.7 (C-23), 70.6 (C-15), 70.3 (C-10), 70.3 (C-5), 39.0 (C-21), 24.3 (C-20), 23.8 (C-16), 23.1 (C-24), 15.2 (C-17), 11.2 (C-19), −3.4 (C-18). FTIR-ATR: ν 2580 (i, B−H str) cm^{-1}. Elem anal. Calcd for $C_{305}H_{583}B_{160}N_4O_{28}Si_{16}Zn$: C, 52.34; H, 8.40; N, 0.80. Found: C, 53.06; H, 8.53; N, 0.75.

2e*$_{Zn}$*-MeCb. The title compound was obtained from **2e**$_{Zn}$ (38 mg, 0.0076 mmol), 1-CH_3-2-[$CH_2CH_2CH_2(CH_3)_2SiH$]-1,2-*closo*-$C_2B_{10}H_{10}$ (109 mg, 0.422 mmol), and 17 μL of Karstedt's catalyst in 1 mL of 1,4-dioxane stirred at 60 °C for 5 h. The reaction mixture was purified by preparative TLC (acetonitrile) and precipitated with 1:1 dichloromethane/ethanol, giving a purple solid (74 mg, 74% yield). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 9.11 (s, 8H, H-β), 7.56 (s, 8H, H-2), 7.12 (s, 4H, H-4), 6.80 (s, 16H, H-7), 6.55 (s, 8H, H-9), 6.53 (s, 32H, H-12), 6.36 (s, 8H, H-14), 5.17 (br s, 8H, H-5), 4.95 (br s, 32H, H-10), 3.85 (br s, 64H, H-15), 2.11 (br s, 64H, H-21), 1.93 (s, 96H, H-24), 1.71 (m, 64H, H-16), 1.52 (m, 64H, H-20), 0.58 (br s, 64H, H-17), 0.50 (br s, 64H, H-19), −0.01 (s, 192H, H-18). ^{11}B NMR ($CDCl_3$, 96.7 MHz): δ −6.01 (d, 64B, $^1J_{B,H}$ = 153 Hz), −10.69 (d, 256B, $^1J_{B,H}$ = 123 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.5 MHz): δ 160.4 (C-13), 158.7 (C-8), 158.0 (C-3), 150.1 (C-α), 139.3 (C-6), 139.0 (C-11), 132.2 (C-β), 107.5 (C-2), 106.7 (C-7), 105.9 (C-12), 102.2 (C-4), 101.7 (C-9), 100.9 (C-14), 78.2 (C-22), 74.7 (C-23), 71.5 (C-5), 70.5 (C-15), 70.2 (C-10), 38.9 (C-21), 24.3 (C-20), 23.8 (C-16), 23.1 (C-24), 15.1 (C-17), 11.1 (C-19), −3.5 (C-18). FTIR-ATR: ν 2580 (i, B−H str) cm^{-1}. Elem anal. Calcd for $C_{564}H_{1132}B_{320}N_4O_{56}Si_{32}Zn$: C, 50.97; H, 8.58; N, 0.42. Found: C, 51.30; H, 8.61; N, 0.44.

Diffusion NMR. All DOSY NMR experiments were carried out on dilute $CDCl_3$ solutions.[67,68] Similar concentrations (about 2 mg of product dissolved in 0.6 mL of $CDCl_3$ into a 5 mm NMR tube) were used to minimize the effect of different solution viscosities for different samples, which were confirmed from the diffusion coefficient of the residual $CDCl_3$ signal taken as an internal reference. After introduction of the sample into the magnet, 10 min were allowed to pass to achieve a general temperature stabilization and regulation along the entire NMR tube. This is important to minimize convection effects highly probable in a nonviscous solvent such as $CDCl_3$.

DOSY experiments were performed at 298 K on a Bruker AVANCE 500 NMR spectrometer operating at 500.13 MHz and equipped with a cryoprobe *z*-gradient inverse probehead capable of producing gradients in the *z* direction with a maximum strength of 53.5 G cm^{-1}. To check for the presence and effective suppression of deleterious convection effects, a test LEDBP experiment was recorded for the first sample with and without sample rotation, and the results were compared to data obtained from double-stimulated echo sequence. Thus, we decided to run DOSY experiments for all samples using the double-stimulated echo sequence incorporating bipolar gradient pulses and a longitudinal eddy current delay (dstegp3s in the Bruker library).

The gradient strength was linearly incremented in 16 steps from 2% up to 95% of the maximum gradient strength. Diffusion times and gradient pulse durations were optimized for each experiment in order to achieve a 95% decrease in the resonance intensity at the largest gradient amplitude; typically, diffusion times between 100 and 150 ms and bipolar rectangular gradient pulses between 1.0 and 2.0 ms were employed. The longitudinal eddy current delay was held constant to 5 ms, whereas the gradient pulse recovery time was set to 100 μs. After Fourier transformation followed by the same phase and baseline correction of each 1D data set, the diffusion dimension of the 2D DOSY spectra was obtained by using the DOSY protocol included into the Bruker *TOPSPIN* software package (version 1.3).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Procedures, ^{1}H, ^{13}C, and HSQC NMR spectra for starting dendrimers, ^{1}H and ^{13}C NMR spectra for carboranyl-containing dendrimers, molecular structures for carboranyl-containing dendrimers, UV−vis spectra for starting dendrimers, and 2D DOSY spectra for dendrimers. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

‡J.C.-G. is enrolled in the UAB Ph.D. program, and E.X.-F. is enrolled in the UNAM Ph.D. program.

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