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Article

“Click” Synthesis and Properties of Carborane-Appended Large Dendrimers

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Large dendrimers, noted G_n-3^{n+2}cage, containing 3^{n+2} *o*-carborane cluster cages $MeC_2B_{10}H_{10}$ at their peripheries (n = number of generation noted G_n) have been synthesized by Huisgen-type azide alkyne Cu^I-catalyzed dipolar “click” cycloaddition reactions (CuAAC) between an *o*-carborane monomeric cluster containing an ethynyl group and arene-centered azido-terminated dendrimers G_n-$3^{n+2}N_3$ of generations 0, 1, and 2. Attempts to synthesize higher-generation dendrimers of this family yielded insoluble materials. The carborane dendrimers G_0-9cage, G_1-27cage, and G_2-81cage have been characterized by ^1H, ^{13}C, ^{11}B NMR, elemental analysis, matrix-assisted laser desorption/ionization time of flight (MALDI-TOF) mass spectroscopy, and size exclusion chromatography (SEC) showing low polydispersities, dynamic light scattering (DLS) showing hydrodynamic diameters of 5.7 nm for the G_1-27cage and the 12.9 nm for the G_2-81cage. These dendrimers are extremely robust thermally, with 10% mass loss temperatures of 411 °C for the G_0-9cage, 371 °C for the G_1-27cage, and 392 °C for the G_2-81cage. They all showed a strong absorption in the UV region peaking at 258 nm, whereas emission spectra of low intensities were observed between 280 and 480 nm.

Introduction

Polymeric and dendritic carborane clusters are useful for a number of applications in nanomedicine,[1] materials science,[2] and organometallic chemistry.[3] The dendritic strategy that consisted in loading a large number of boron atoms in a dendritic molecule has been pioneered by Newkome et al. who introduced 12 boron cluster termini at the periphery of arborol tethers.[4,5] This goal was further explored successfully by introducing six high boron-containing carboranes in star molecules bearing peripheral carboranes[6] or in small dendrimers containing up to 12 *o*-carborane clusters.[7] Grimes also reported a remarkable dendrimer containing 128 boron atoms.[8] Large dendrimers encapsulating carboranes have been recently reported for boron neutron capture therapy (BNCT) application with a G_5-PAMAM dendrimer.[9] One of our groups has recently reported star hexacarboranes and small dendrimers containing 12 carboranes.[6,10] The thermal stability of small star-shaped hexacarboranyl dendrimers and sandwiched hexametallacarboranyl dendrimers, prepared by one of our groups,[6,10] also contributed to rekindle our interest in exploring new synthetic strategies for the construction of large carborane-appended dendritic molecules and to study their reactivity patterns.

Huisgen-type azide alkyne Cu^I-catalyzed dipolar “click” cycloaddition reactions (CuAAC) have recently proved invaluable for connecting organic and bioorganic segments and

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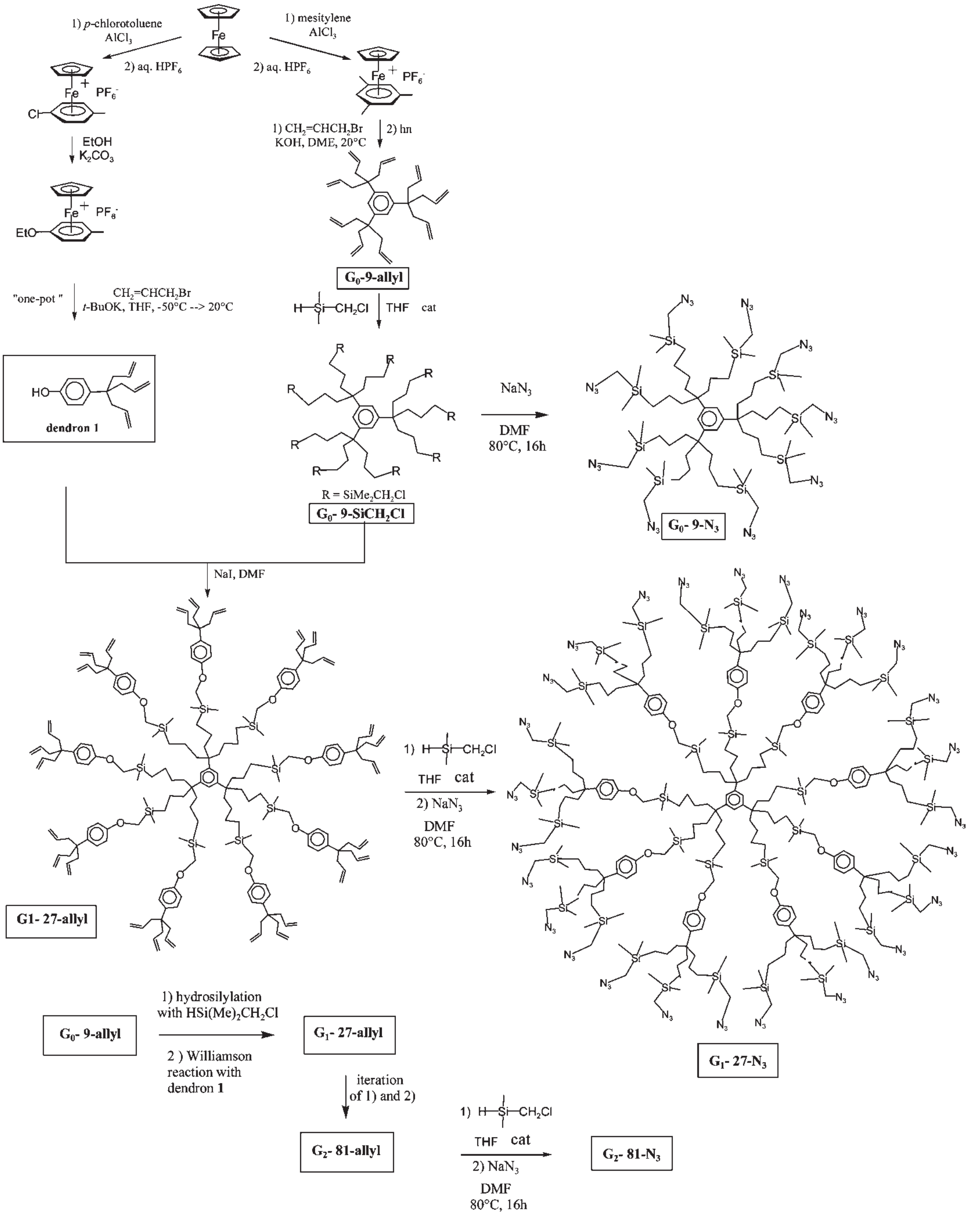
Scheme 1. General Scheme for the Synthesis of the Dendrimers G_n-3^{n+2}-N_3 (Generation Numbers n = 0−2) Used for the "Click" Reactions[a]



[a] See also references12−18, and 20.

functions.[11,12] We wish to report here the "click" synthesis, spectroscopic and analytical characterization, and thermal stability of large arene-centered dendrimers with up to 81 *o*-carborane cluster termini $MeC_2B_{10}H_{10}$, that is, 810 B atoms *per* dendrimer molecule.

Results and Discussion

1. Synthesis of the Organic Precursors. Arene-centered dendrimers have been synthesized as previously reported by η^5-$C_5H_5Fe^+$-induced nona-allylation of mesitylene,[13] followed by photochemical decomplexation using visible light,[14] hydrosilylation of the terminal double bonds with chloromethyldimethylsilane, and Williamson reaction with the phenoltriallyl dendron p-HO-$C_6H_4C(CH_2CH{=}CH_2)_3$

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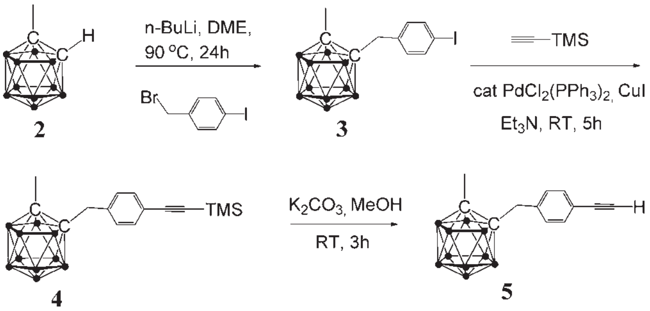
Scheme 2. Synthesis of the Functionalized Carborane Cluster **5** with a Terminal Alkyne Group



yielding a 27-allyl dendrimer.[15] Reiteration of the hydrosilylation with chloromethyldimethylsilane and subsequent Williamson reaction with this dendron yielded the known dendrimers containing 3^{n+2} allyl termini, n being the generation number.[16] Terminal functionalization with azido groups could be achieved by nucleophilic substitution of the terminal chloro group of the chloromethylsilyl-terminated dendrimers of generations 0−2 (G_0-G_2) with sodium azide (Scheme 1), which allowed to carry out "click" reactions at the periphery of dendrimers with terminal alkynes.[17] This strategy has recently led to 1,2,3-triazolyferrocenyl dendrimers up to G_2 with $3^4 = 81$ termini.[12,18] Here, we are using these azido-terminated dendrimers for "click" reactions with a carborane that is functionalized with an alkyne group.

This alkyne precursor **5** used for the "click" reactions and containing the *o*-carborane cluster $MeC_2B_{10}H_{10}$ was synthesized by deprotonation of 1-methyl-*o*-carborane, **2**, with *n*-BuLi, followed by benzylation of the resulting carborane anion using p-I−$C_6H_4CH_2Br$, giving **3**, which was subsequently coupled with trimethylsilylacetylene using the Sonogashira coupling catalyzed by $PdCl_2(PPh_3)_2$ and CuI in the presence of triethylamine, and finally deprotection of this alkyne **4** using K_2CO_3 in methanol (Scheme 2).

2. "Click" Synthesis of the Carborane-Terminated Dendrimers. The Cu^I-catalyzed alkyne azide 1,3-dipolar cycloaddition (CuAAC) was carried out between the alkyne **5** and the three dendrimers G_0-$9N_3$, G_1-27 N_3, and G_2-$81N_3$ using a stoichiometric amount of Cu^I generated from $CuSO_4$ and sodium ascorbate in water-tetrahydrofuran (THF, 1:1) mixture (Schemes 3 and 4, Charts 1 and 2).

Attempts to carry out such reactions with higher azido-terminated dendrimers (G_3-$243N_3$ and G_4-$729N_3$) resulted in the formation of insoluble materials presumably resulting from steric saturation at the dendrimer periphery,[19] and further analyses of these insoluble materials were not performed.

With G_0-G_2, the reaction mixture changed color from brown at 0 °C to yellow at room temperature. The reaction was not complete with catalytic amounts of Cu^I, that were not sufficient, as in previous "click" reactions involving dendrimers, presumably because of encapsulation of Cu^I by coordinating to the resulting 1,2,3-triazolyl ligand.[12,18] The copper salt was finally removed after stirring with an aqueous NH_3 solution as $[Cu(NH_3)_2(H_2O)_2]$ $[SO_4]$. The resulting carborane-terminated dendrimers were purified, after workup, by precipitation using methanol from dichloromethane (DCM) solutions. They were characterized by ^1H, ^{13}C, and ^{11}B NMR, IR, UV−vis, matrix-assisted laser desorption/ionization time of flight (MALDI-TOF) mass spectroscopies, and elemental analysis. The IR spectra of dendrimers containing *o*-carborane clusters showed strong bands between 2574 and 2584 cm^{-1} corresponding to ν (B−H). The ^{11}B NMR spectra of carborane-appended dendrimers showed peaks between −5.78 and −10.63 ppm indicating the presence of *o*-carborane clusters.[6,10] Size exclusion chromatography (SEC, Figure 1) showed very low polydispersity indices (PDI = 1.01 for G_0 and G_1, and 1.05 for G_2). These low polydispersity values were measured for the signal of each dendrimer only and do not take into account the side signals of low intensities because of agglomerated dendrimers that are visible in Figure 1. Dynamic light scattering (DLS) measurements for G_1 and G_2 indicated hydrodynamic diameters of 5.7 nm for G_1-27cage and 12.9 nm G_2-81cage, and Table 1 shows the DLS data together with the calculated diffusion coefficients, volumes and densities of the carborane dendrimers. Finally, the MALDI-TOF mass spectral data of G_0-9cage, G_1-27cage, and G_2-81cage dendrimers confirmed their formation. The MALDI-TOF mass spectral data for the G_0-9cage dendrimer showed a sharp peak at m/z 3960.7 against the exact molecular weight m/z 3963.2, whereas for the dendrimers containing larger number of cages broad bands were observed around the exact molecular weight. For the G_1-27cage dendrimer a broad band was observed between m/z 8268−13849 peaking at m/z 11385 against the exact molecular weight m/z 13650.7. Similarly for the G_2-81cage dendrimer a broad band was observed between m/z 21311−104535 peaking at m/z 48000 against the exact molecular weight m/z 42695.2 (see the Supporting Information). The relatively broad distribution observed for G_1-27 and G_2-81 is due to the isotope distribution of boron atoms and the presence of high numbers of boron atoms in these molecules.

3. Thermal Properties. Recent investigations on the thermal properties of carborane-appended compounds have led to a conclusion that incorporation of multiple carborane clusters make the compound highly thermally stable.[6,10] A systematic thermal analysis of polycarborane dendrimers also gave similar results, and these compounds

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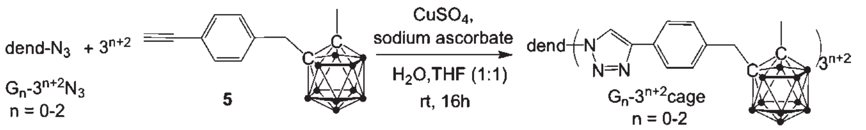
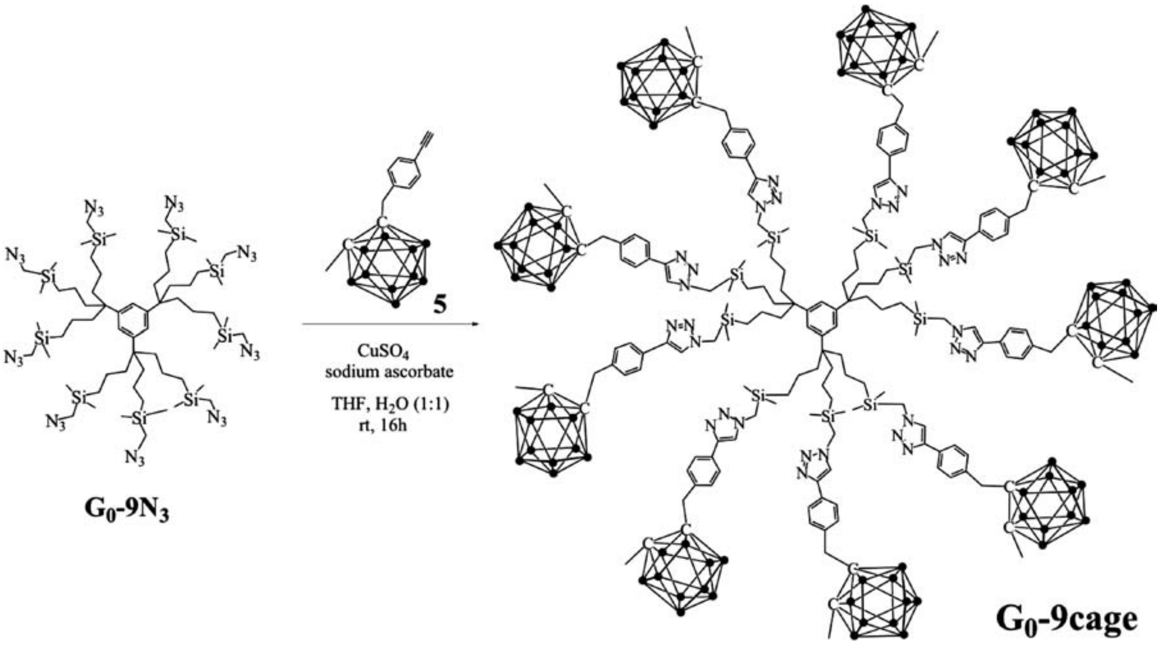
Scheme 3



Scheme 4



are found to be thermally very robust (Figure 2). The temperatures at which 10% mass loss of all the dendrimers occurred are summarized in Table 2. For the G_0-9cage dendrimer that contains nine *o*-carborane clusters, the point at which 10% mass loss occurred is found to be 411 °C, and finally about 32-weight % of the residue is maintained at 600 °C. For the G_1-27cage dendrimer, that contains 27 *o*-carboranes, the 10% mass loss occurs at 371 °C, and about 18-weight % of the residue is maintained at 600 °C. The G_2-81cage dendrimer that contains eighty-one C_{cage}-appended *o*-carboranes, the 10% mass loss occurred at 392 °C, and about 24-weight % of the residue is maintained at 600 °C. The G_0-9cage dendrimer is found to be the most stable compound in the series. The result is consistent with the boron content of the dendrimers. The G_0-9cage dendrimer has the highest boron content that is about 24.5%, whereas the dendrimers G_1-27cage and G_2-81cage possess about 21 and 20.5% boron by weight respectively. In addition, G_0-9cage does not contain the phenolate linkage that is relatively fragile, whereas the larger dendrimers do, which favors G_0-9cage in terms of thermal stability. Finally, a dendrimer effect seems to better stabilize G_2-81cage compared to G_1-27cage. Further, it should be noted that these carborane-appended dendrimers are still less thermally stable than recently reported cobaltabisdicarbollides for which only a 10−30% mass loss occurs at 700 °C.[10]

4. Photophysical Properties. Recently, the incorporation of *o*-carborane clusters into π-conjugated compounds was reported to result in enhanced emission intensity.[6,10] However, the dendrimers described here are not found to be fluorescent compounds. Although these dendrimers contain multiple phenyl rings, they are not conjugated. Thus, a strong absorption band was observed for all dendrimers peaking at 258 nm, and emission spectra of lower intensity were observed between 280 and 480 nm for all three dendrimers (Figure 3).

Concluding Remarks

Huisgen-type azide alkyne Cu^I-catalyzed dipolar "click" cycloaddition reactions (CuAAC) between a *o*-carborane monomeric cluster containing an ethynyl group and arene-centered azido-terminated dendrimers G_n-$3^{n+2}N_3$ of generations 0, 1, and 2 have proved to be very facile, leading to well-characterized, thermally robust *o*-carborane-containing dendrimers. Higher-generation analogues were prepared, but their insolubility in all solvents, presumably because of steric saturation at the dendrimer peripheries, precluded their characterization. It is likely that the tether-lengthening strategy recently used for the synthesis of dendritic molecular batteries and that led to metallodendrimers containing up to 14,000 metallocenyl termini (Fe, Co)[21] might also push the limit of carborane dendrimer syntheses far beyond the current limit. Such a goal is important in view of the requirement of high content of boron atoms in a small nanospace for boron neutron capture therapy.[1,2] Nevertheless, this useful "click" strategy has produced here among the largest characterized

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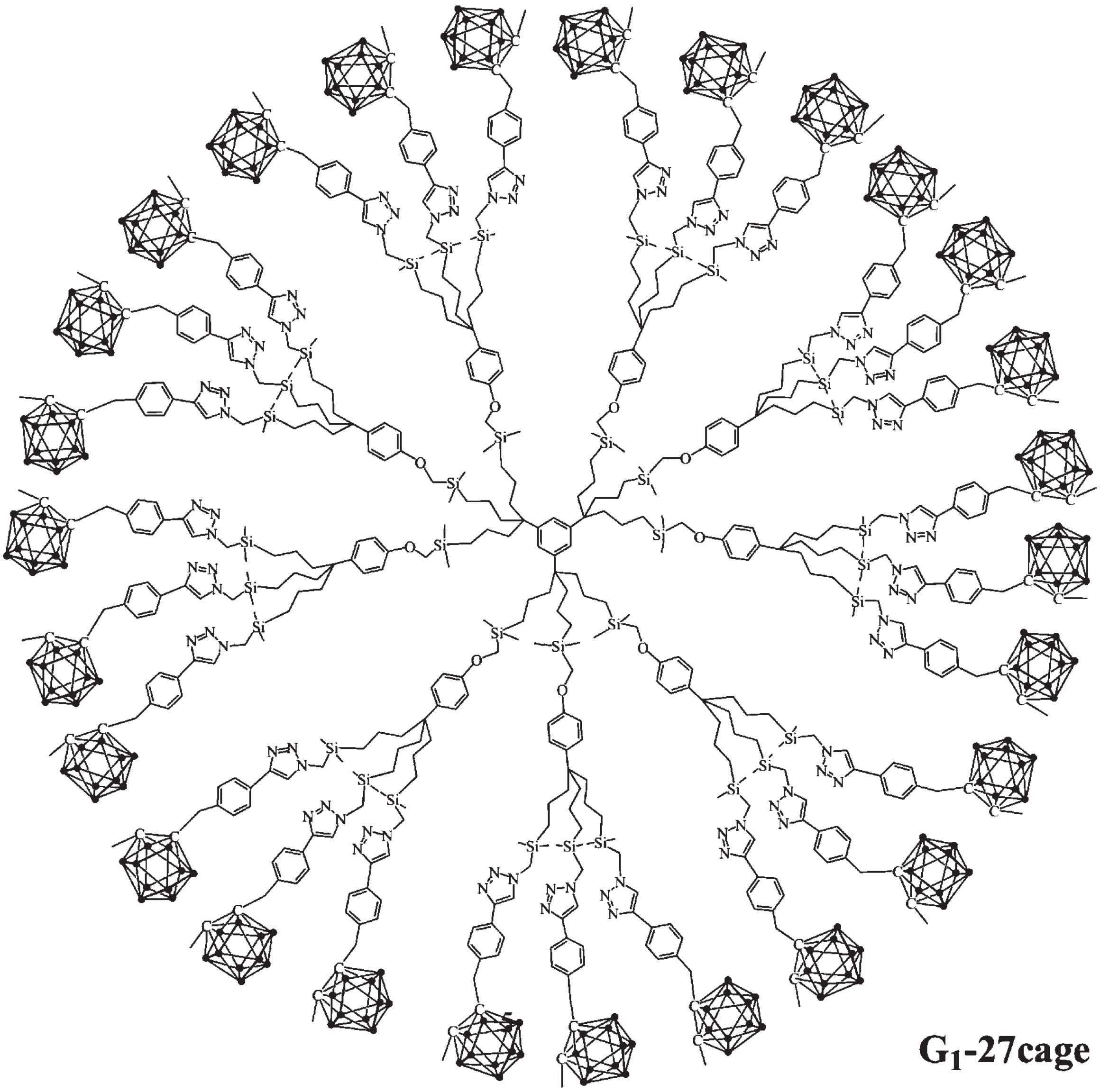
Chart 1



G_1-27cage

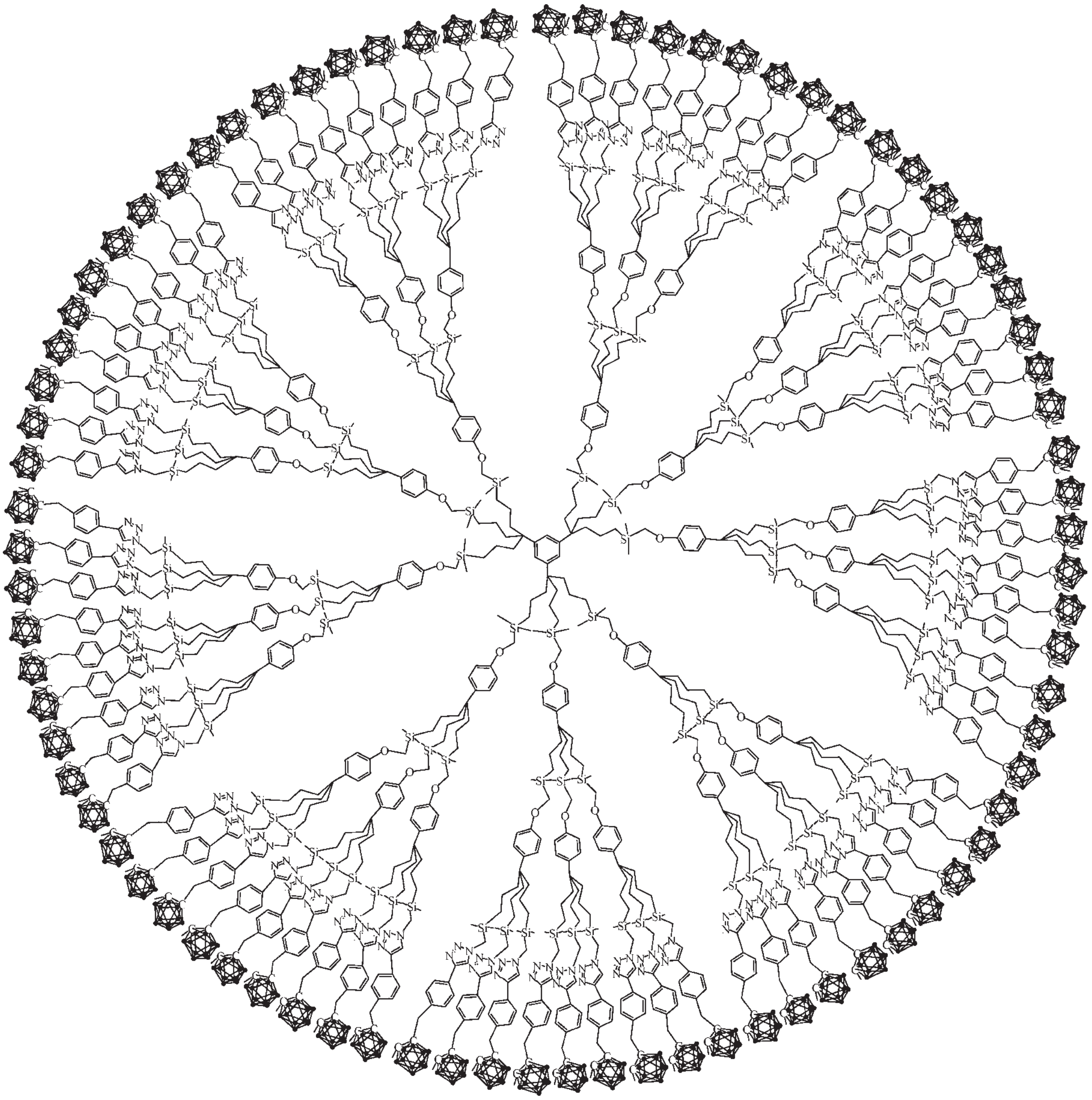
carborane dendrimers known to-date with up to 810 boron atoms in a single molecule.

Experimental Section

General Data. Reagent-grade diethyl ether, dimethoxyethane (DME) and tetrahydrofuran (THF) were predried over Na foil and distilled from sodium-benzophenone anion under argon immediately prior to use. Dichloromethane (DCM) was distilled from calcium hydride just before use. All other solvents (hexane, methanol) and chemicals were used as received. The Kartsted catalyst and anhydrous DMF were purchased from Aldrich. ^{1}H NMR spectra were recorded at 25 °C with a Bruker AC 200, 300, or 500 (200, 300, or 500 MHz) spectrometer. The ^{13}C NMR spectra were obtained in the pulsed FT mode at 50, 75, or 125 MHz with a Bruker AC 200, 300, or 500 spectrometer, and the ^{11}B NMR spectra were recorded at 160.5 MHz with a Bruker AC 500 relative to $BF_3 \cdot Et_2O$. All chemical shifts are reported in parts per million (δ, ppm) with reference to Me_4Si (TMS) for the ^{1}H and ^{13}C NMR spectra and with reference to $BF_3 \cdot Et_2O$ for the ^{11}B NMR spectra. The mass spectra were recorded using an Applied Biosystems Voyager-DE STR-MALDI-TOF spectrometer. The DLS measurements were made using a Malvern Zetasizer 3000 HSA instrument at 25 °C at an angle of 90°. Infrared spectra were recorded on an ATI Mattson Genesis series FT-IR spectrophotometer. UV absorption and emission spectra were measured with Perkin-Elmer Lambda 19 UV−vis spectrometer and Hitachi F-2500 Fluorescence spectrophotometer, respectively. Thermal gravimetric analysis (TGA) was performed on a Perkin-Elmer Pyris 1 analyzer at a heating rate of 5 °C/min under argon. The elemental analyses were performed by the Center of Microanalyses of the CNRS at Lyon Villeurbanne, France. The dendrimers G_0-$9N_3$, G_1-$27N_3$, and G_2-$81N_3$ were synthesized according to references 12 and 18. The dendron **1** was synthesized according to references 15 and 20. 1-Me-*o*-carborane **2** was prepared using a previously reported procedure.^{6}

Carborane Derivative 3. 1-Methyl-*o*-carborane, **2**, (1.4 g, 8.86 mmol) was solubilized in 60 mL of dry DME), then *n*-BuLi (1.6 M in hexanes, 6.64 mL, 10.63 mmol) was added to it at 0 °C. This reaction mixture was stirred at 0 °C for 1 h, and a solution of 4-iodo benzyl bromide (2.10 g, 7.08 mmol) in 5 mL of DME was added at 0 °C. The reaction mixture was refluxed at 100 °C for 24 h, then cooled to room temperature, and filtered over a short silica gel column. Recrystallization in hexane/dichloromethane yielded 2.1 g (65%) of the pure compound **3**. M.P: 123 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.71 (d, 2H, J = 8.0 Hz),

Chart 2



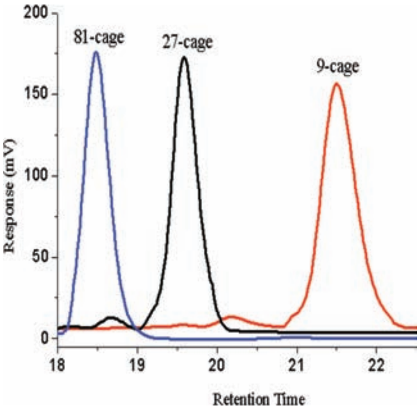


Figure 1. Size exclusion chromatograms of the carborane dendrimers. Red line, G_0-9cage; black line, G_1-27cage; blue line, G_2-81cage. The polydispersities indices (PDI) are 1.01 (G_0-9cage), 1.01 (G_1-27-cage), and 1.05 (G_2-81-cage).

6.96 (d, 2H, J = 8.0 Hz), 3.42 (s, 2H), 2.17(s, 3H cluster-CH_3).^{13}C NMR ($CDCl_3$, 125 MHz): δ 137.7, 134.5, 132.1, 93.9, 76.8 (C_{cage}), 74.8 (C_{cage}), 40.7, 23.7. ^{11}B NMR ($CDCl_3$, proton decoupled, 64.2 MHz): δ −3.98 (1 B), −5.50 (1 B), −10.1 (8 B). $B_{10}C_{10}H_{17}I$: calcd. C 32.26, H 4.60; found C 32.28, H 4.59.

Carborane Derivative 4. To a mixture of compound **3** (3.0 g, 8.01 mmol) in 40 mL of dry THF and 40 mL of Et_3N, $[PdCl_2(PPh_3)_2]$ (224 mg, 0.32 mmol), CuI (76.2 mg, 0.4 mmol), ethynyltrimethylsilane (1.67 mL, 12.02 mmol) were added at room temperature (rt). The reaction mixture was then stirred at rt overnight, then filtered over a silicagel pad. After evaporation of the solvent, the crude reaction product was purified by silica gel column chromatography with hexane as eluent, which gave 2.48 g of pure compound **4** as a colorless solid. Yield: 90%. M.P: 98 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.47(d, 2H, J = 8.0 Hz), 7.14(d, 2H, J = 8.0 Hz), 3.45(s, 2H), 2.16 (s, 3H, cluster-CH_3), 0.28(s, 9H, $SiMe_3$).^{13}C NMR ($CDCl_3$, 125 MHz): δ 135.2, 132.1, 130.2, 123.0, 104.3, 95.3, 77.1(C_{cage}), 74.8(C_{cage}), 41.0, 23.6, −0.0., ^{11}B NMR ($CDCl_3$, proton decoupled, 64.2 MHz): δ −4.03 (1 B), −5.52 (1 B), −10.11 (8 B). IR (KBr): 2959, 2594, 2898, 2162, 1505, 1462, 1250, 1020 cm^{-1}. $B_{10}C_{15}H_{28}Si$: calcd. C 52.28, H 8.19; found C 52.11, H 7.93.

Carborane Derivative 5. Compound **4** (2.2.g, 6.37 mmol) was dissolved in 20 mL of THF and 20 mL of MeOH, then K_2CO_3 (968 mg, 7.01 mmol) was added, and the mixture was stirred at rt

Table 1. Hydrodynamic Diameters ($2\times R_h$) Determined by DLS, and Calculated Volumes, Diffusion Coefficients, and Densities for G_1-27cage and G_2-81cage

product[a]	MM[b]	$2 \times R_h$[c]	D ($m^2.s^{-1}$)[d]	volume[e](m^3)	d[f]
9-cage	3963				
27-cage	13693	5.7 ± 0.8	17×10^{-14}	$(0.97 \pm 0.44) \times 10^{-25}$	230 ± 100
81-cage	42821	12.9 ± 2.0	7.4×10^{-14}	$(11.2 \pm 5.0) \times 10^{-25}$	63 ± 28

[a] The hydrodynamic diameter of G_1-9cage could not be obtained by DLS because it is below the lower limit of the technique. [b] MM: molecular mass (g mol^{-1}·). [c] $2\times R_h$: hydrodynamic diameter (nm) measured in THF at 25 °C. [d] D: diffusion coefficient (m^2 s^{-1}). [e] considering the globular shape of the dendrimer as a perfect sphere ($V = (4/3)\pi R_h^3$) [f] d: density (kg/m^3).

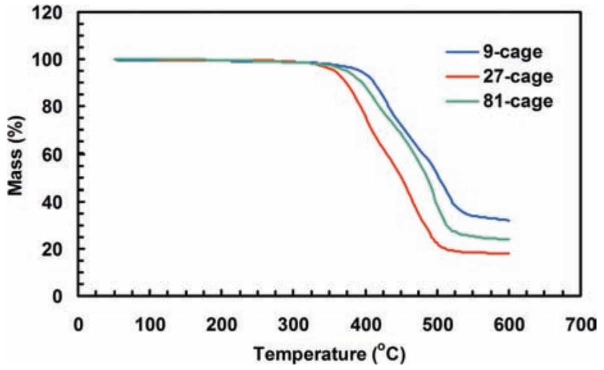


Figure 2. Thermogravimetric analysis (TGA) curves of carborane dendrimers under argon. Blue line, G_0-9cage; red line, G_1-27cage; green line, G_2-81cage.

Table 2. 10% Mass Loss Temperatures from TGA

dendrimers	temperature (°C)
G_0-9cage	411
G_1-27cage	371
G_2-81cage	392

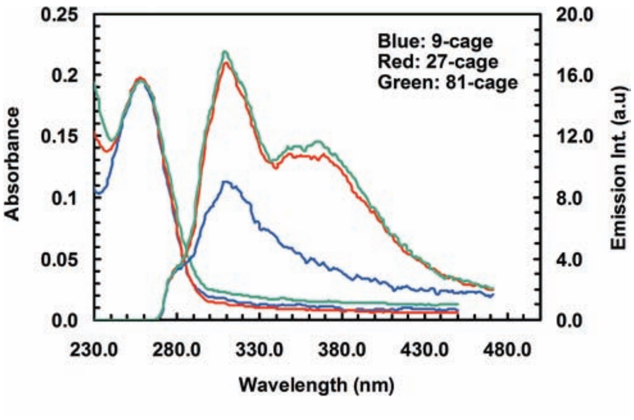


Figure 3. Absorption and emission spectra of the carborane dendrimers in DCM. Bluelines, G_0-9cage; red lines, $G_1$27cage; green lines, G2−81cage.

for 5 h. The crude reaction mixture was filtered over a cotton plug. After evaporation of the solvent under vacuum, the crude reaction product was purified by silica gel column chromatography with 20% ethyl acetate in hexane as eluent, giving 1.66 g of pure compound **5** as a colorless solid. Yield: 95%. M.P: 120 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.50 (d, 2H, J = 8.0 Hz), 7.17(d, 2H, J = 8.0 Hz), 3.47(s, 2H), 3.14 (s, 1H), 2.17(s, 3H cluster-CH_3). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 135.6, 132.3, 130.3, 122.0, 83.0, 78.1(C_{cage}), 77.0(C_{cage}), 74.9, 41.0, 23.6. ^{11}B NMR ($CDCl_3$, proton decoupled, 64.2 MHz): δ −3.95 (1 B), −5.53 (1 B), −10.0 (8 B). IR (KBr): 3049, 2933, 2563, 2107, 1507, 1237, 1153, 1028 cm^{-1}. $B_{10}C_{12}H_{20}$: calcd. C 52.91, H 7.40; Found C 52.93, H 7.31. HRMS (ES) (m/z): calcd for $B_{10}C_{12}H_{20}$: 274.2495; Found 274.2496.

General Procedure for the "Click" Synthesis of the Polycarborane Dendrimers G_n-3^{n+2}cage, (n = 0, 1, 2). The compound **5** (1.5 equiv *per* branch) and the azido-terminated dendrimer were dissolved in 50 mL of degassed THF, then 50 mL of degassed water was added; then the reaction mixture was cooled to 0 °C, and an aqueous solution of $CuSO_4$ 1 M (1 equiv *per* branch, THF-H_2O, 1:1) was added at 0 °C, followed by the dropwise addition of a freshly prepared solution of sodium ascorbate 1 M (2 equiv *per* branch). The color of the solution, that was brown at 0 °C, changed to yellow at rt. The reaction mixture was allowed to stir for 24 h under nitrogen atmosphere at rt. Then, 100 mL of DCM was added, followed by the addition of an aqueous solution of ammonia. The mixture was allowed to stir for10 min to remove all the copper salt $[Cu(H_2O)_2(NH_3)_2][SO_4]$ trapped inside the dendrimer. The organic phase was washed twice with water, dried over sodium sulfate, filtered, and the solvent was removed under vacuum. The product was then washed with methanol to remove the excess alkyne and precipitated from a DCM solution with methanol.

Dendrimer G_0-9cage. The synthesis was carried out from ethynylcarborane (0.121 g, 0.445 mmol) and G_0-$9N_3$ (0.050 g, 0.033 mmol) using the general procedure for the "click" synthesis of the polycarboranes G_n-3^{n+2}cage, (n = 0−2). The nonacarborane G_0-9cage was obtained as a colorless dusty powder (0.110 g, yield 85%). ^{1}H NMR ($CDCl_3$, 200 MHz), δ_{ppm}: 7.77 (d, 18H, arom-cluster), 7.75 (s, 9H of triazole), 7.18 (d, 18H, arom.), 6.97 (s, 3H, CH core), 3.89 (s, 18H, SiCH_2-triazole), 3.44 (s, 18H, cluster-CH_2-), 2.16 (s, 27H, cluster-CH_3), 1.62 (s, 18H, C$H_2$$CH_2CH_2$Si), 1.09 (s, 18H, CH_2C$H_2$$CH_2$Si), 0.62 (s, 18H, $CH_2CH_2CH_2$Si), 0.09 (s, 54H, $Si(CH_3)_2$). ^{13}C NMR ($CDCl_3$, 50 MHz), δ_{ppm}: 146.5 (Cq-triazole), 145.7 (Cq-core), 134.5 (Cq of Ar-cluster), 130.7 and 125.5 (CH of Ar-cluster), 121.6 (CH of arom. core), 121.0 (CH-triazole), 77.4 and 75.0 (C of cluster) 43.9 (Cq$C$$H_2CH_2CH_2$Si), 41.7 ($CqCH_2CH_2CH_2$Si), 41.3 (triazole-$C$$H_2$Si), 40.8 (cluster-$C$$H_2$−Ar), 23.5 (cluster-$C$$H_3$), 17.5 (Cq$CH_2$$C$$H_2CH_2$Si), 14.9 (Cq$CH_2CH_2$$C$$H_2$Si), −3.8 ($Si(CH_3)_2$). ^{11}B NMR ($CDCl_3$, proton decoupled, 160.5 MHz): δ −5.78 (18 B), −10.42 (72 B). IR (KBr): 2926, 2584 (B−H), 1494, 1372, 1256, 814 cm^{-1}. MALDI-TOF-MS (m/z): calcd 3963.2; found 3960.7 (M^+-2, 100%). Anal. Calcd for $C_{171}H_{309}B_{90}Si_9N_{27}$: C 51.54, H 7.76 ; found: C 50.83, H 7.91.

Dendrimer G_1-27cage. The dendrimer G_1-27cage was synthesized from ethynylcarborane (0.088 g, 0.322 mmol) and G_1-$27N_3$ (0.050 g, 0.008 mmol) using the general procedure for the "click" synthesis of the polycarboranes G_n-3^{n+2}carborane, (n = 0−2). The dendrimer G_1-27cage was obtained as a colorless dusty powder (0.088 g, yield 81%). ^{1}H NMR ($CDCl_3$, 200 MHz), δ_{ppm}: 7.77 (d, 54H, arom.), 7.67 (s, 27H of triazole), 7.19 (m, 72H, arom. and Ar-cluster), 6.89 (d, 18H, CH core), 3.88 (s, 54H, SiCH_2-triazole), 3.53 (s, 18H, OCH_2Si), 3.44 (s, 54H, cluster-CH_2-), 2.15 (s, 81H, cluster-CH_3), 1.58 (s, 72H, C$H_2$$CH_2CH_2$Si), 1.09 (s, 72H, CH_2C$H_2$$CH_2$Si), 0.60 (s, 72H, CH_2CH_2CH_2Si), 0.06 (s, 216H, Si(CH_3)$_2$). ^{13}C NMR ($CDCl_3$, 50 MHz), δ_{ppm}: 159.0 (arom. OCq), 146.5 (Cq-triazole), 138.7 (arom. Cq), 134.5 (Cq of Ar-cluster), 130.7 and 125.5 (CH of Ar-cluster), 127.0 and 113.4 (arom. CH of dendron), 120.6 (CH-triazole), 77.4 and 74.8 (C of cluster), 60.3 ($C$$H_2$OAr), 42.8 (Cq$C$$H_2CH_2CH_2$Si), 41.6 ($CqCH_2$-$CH_2CH_2$Si), 40.9 (triazole-$C$$H_2$Si), 40.8 (cluster-$C$$H_2$−Ar), 23.5 (cluster-$C$$H_3$), 17.3 (Cq$CH_2$$C$$H_2CH_2$Si), 14.7 (Cq$CH_2CH_2$$C$$H_2$Si), −3.9 ($Si(CH_3)_2$). ^{11}B NMR ($CDCl_3$, proton decoupled, 160.5

MHz): δ −5.84 (54 B), −10.42 (216 B). IR (KBr): 2931, 2581 (B−H), 1506, 1403, 1250, 814 cm^{-1}. MALDI-TOF-MS (*m*/*z*): calcd 13650.7; found a broad band between 8268 and 13849 peaking at 11385. Anal. Calcd for $C_{612}H_{1083}B_{270}Si_{36}N_{81}O_9$: C 53.67, H 7.91; found: C 53.68, H 8.15.

Dendrimer G$_2$-81cage. The dendrimer G$_2$-81cage was synthesized from ethynylcarborane (0.081 g, 0.298 mmol) and G$_2$-81N$_3$ (0.050 g, 0.0025 mmol) using the general procedure for the “click” synthesis of the polycarboranes G$_n$-3^{n+2}carborane, (n = 0−2). The dendrimer G$_2$-81cage was obtained as a colorless dusty powder (0.083 g, yield 80%). ^{1}H NMR (CDCl$_3$, 200 MHz), δ_{ppm}: 7.76 (d, 162H, arom.), 7.65 (s, 81H of triazole), 7.19 (m, 234H, arom. and Ar-cluster), 6.87 (d, 72H, CH core), 3.87 (s, 162H, SiCH_2-triazole), 3.50 (s, 72H, OCH_2Si), 3.43 (s, 162H, cluster-CH_2-), 2.13 (s, 243H, cluster-CH_3), 1.58 (s, 234H, CH_2CH$_2$CH$_2$Si), 1.07 (s, 234H, CH$_2$CH_2CH$_2$Si), 0.58 (s, 234H, CH$_2$CH$_2$CH_2Si), 0.09 (s, 702H, Si(CH_3)$_2$). ^{13}C NMR (CDCl$_3$, 50 MHz), δ_{ppm}: 159.0 (arom. O*C*q), 146.5 (*C*q-triazole), 138.8 (arom. *C*q), 134.5 (Cq of Ar-cluster), 130.7 and 125.6 (*C*H of Ar-cluster), 127.0 and 113.5 (arom. *C*H of dendron), 120.7 (*C*H-triazole), 77.6 and 74.9 (C of cluster), 60.1 (*C*H$_2$OAr), 42.9 (Cq*C*H$_2$CH$_2$CH$_2$Si), 41.7 (*C*qCH$_2$CH$_2$CH$_2$Si), 41.0 (triazole-*C*H$_2$Si), 40.8 (cluster-*C*H$_2$−Ar), 23.6 (cluster-*C*H$_3$), 17.5 (CqCH$_2$*C*H$_2$CH$_2$Si), 14.7 (CqCH$_2$CH$_2$*C*H$_2$Si), −3.9 (Si(CH$_3$)$_2$). ^{11}B NMR (CDCl$_3$, proton decoupled, 160.5 MHz): δ −5.86 (162 B), −10.63 (648 B). IR (KBr): 2929, 2574 (B−H), 1503, 1381, 1254, 823 cm^{-1}. MALDI-TOF-MS (*m*/*z*): calcd 42695.2; found a broad band between 21311 and 104535 peaking at 47997. Anal. Calcd for $C_{1935}H_{3405}B_{810}Si_{117}N_{243}O_{36}$: C 54.26, H 7.95; found: C 54.59, H 8.35.

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Supporting Information Available: ^{1}H and ^{13}C NMR, ^{11}B, IR and MALDI-TOF mass spectra of new products (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.