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Synthesis of Calixarene-Capped Carbosilane Dendrimers

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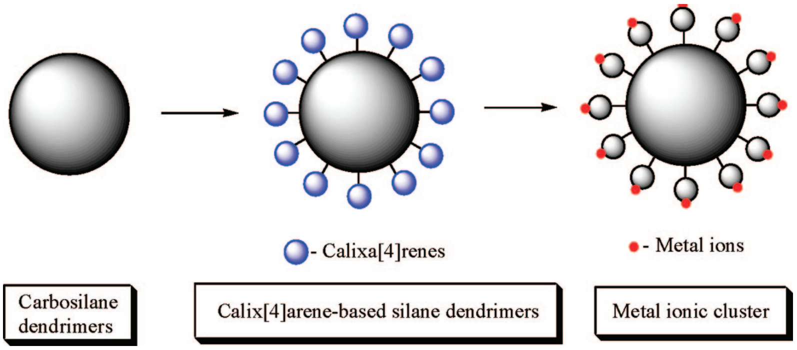

A new class of polycalix[4]arene hosts has been constructed based on a carbosilane dendrimer architecture, in which each dendritic branch terminates with a calix[4]arene entity. This study reports the synthesis and characterization of the zeroth generation example with four calix[4]arenes and of the first generation example with 12 calix[4]arenes.

Introduction

Calixarenes have been an active subject of research since their development by Gutsche.[1−6] Readily accessible synthetically, they can serve as hosts for a wide variety of inorganic cations and organic molecules. As metal binders,[7] they have found uses in catalysis,[8] separations,[9] and chemosensing.[10] Shinkai and co-workers[11] demonstrated that a branched architecture improves and intensifies the ability of calixarenes to bind with metal cations, possibly by creating new or multiple binding sites. Dendrimers have been widely explored for about two decades for a variety of very general applications.[12] Crooks,[13] Tomalia,[14] and their co-workers have used dendrimers with a number of terminal groups to bind copper(II).

To date, there have been limited synthetic approaches to calixarenes with a branched architecture. The largest branched systems contain only five calixarene units: a central calixarene attached to four terminal calixarenes.[11,15,16] Branching occurs only around the core calixarene in these pentacalixarenes, so they are zeroth generation dendrimers. Although Lhotak and Shinkai[11] demonstrated that nondendritic dicalixarenes bind with up to two Li^+ ions, the equilibria of their tri- and

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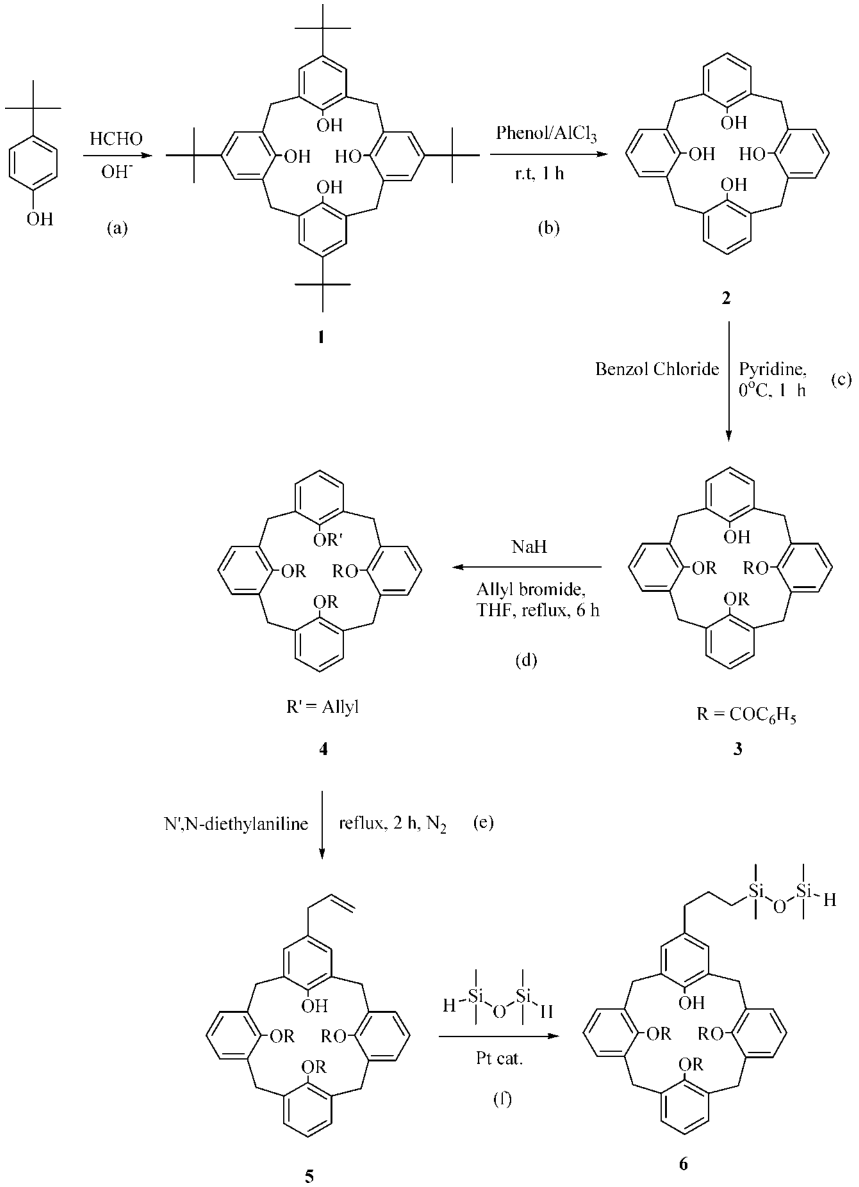
SCHEME 1



pentacalixarenes were characterized only qualitatively. Wang and Gutsche demonstrated that a tricalixarene exhibited cooperative binding with C60.[16] Thus multiple calixarene units can accomplish binding not possible with single units. The only truly dendritic calixarene reported to date, without complexation studies, is a heptacalixarene, in which a core calix[4]arene is attached to two calix[4]arene units.[17] These units serve as 2-fold branch points that lead to a total of four peripheral calix[4]arenes. Polymeric dendrimers also have been reported.[18]

Tomalia, Crooks, and their co-workers[19] used PAMAM [poly(amidoamine)] dendrimers to bind Cu(II). Although these dendrimers have potential internal binding sites, Crooks et al. concluded that Cu(II) binds with terminal amines. Stoichiometry indicated that each copper ion is bound to two terminal amines (thus the second generation binds with 4 copper ions, the fourth with 16, and the sixth with 64). Since PAMAM only doubles the number of binding sites with each generation, very high generations were required before a large number of ions could be bound. In these systems peripheral units seem to be most effective in binding.

It was the purpose of the current study to find an efficient route to calixarene dendrimers as possible substrates to exhibit cooperative and enhanced binding. The dendritic architecture we envisioned is quite different from those of Shinkai,[11] Böhmer,[15] Gutsche,[16] or Beer.[17] The systems of these authors used calixarenes as the core, the branching points (in the single case of Beer's work), and the termini. Interior calixarenes might be less accessible and hence less available for binding. The systems of these authors would be difficult to build up to higher level dendrimers. Our calixarene units are designed to be located only at the dendritic termini and hence should be fully accessible

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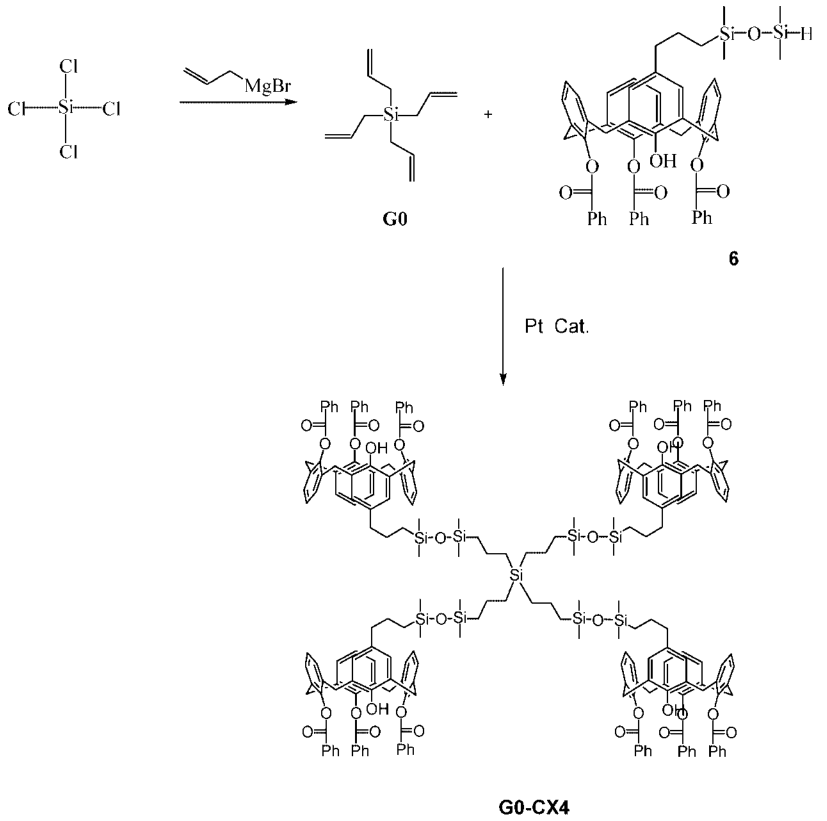
SCHEME 2



to binding. By using a 3-fold branching carbosilane structure[20] (the sole existing dendritic calixarene[17] contains 2-fold branching) we can assemble higher level dendrimers quickly and efficiently. Moreover, the carbosilane interior does not allow binding, in contrast to the linkages of the PAMAM dendrimers. We report herein the successful synthesis and characterization of zeroth and first generation dendrimers that respectively contain 4 and 12 surface calixarene units. These dendrimers provide multiple surface calixarenes capable of potential cooperative binding without competition from interior binding sites.

Results and Discussion

Synthesis. The scheme in the abstract presents the overall strategy of this study. A carbosilane dendrimer of the appropriate generation is prepared with multiple surface functionalities capable of being tied to a calix[4]arene unit, which can bind with a metal cation. A convergent synthesis (eq 1) optimizes the yield, as the calixarene and carbosilane pieces are assembled separately and subsequently are tied together. This approach involves synthesis of two major components, one of which contains a single calixarene (calix-$CH_2CH{=}CH_2$), and the other is the allyl-tipped carbosilane dendrimer [carbosilane$(CH_2CH{=}CH_2)_n$]. These components then are brought together in a ligation step (eq 1), whereby *n* calixarenes are attached to the *n* chains of the dendrimer. We used double hydrosilylation for the ligation process, in which 1,1,3,3-tetramethyldisiloxane (TMDS) is the ligating element.

$$n\,\text{calix-}CH_2CH{=}CH_2 + n\,\text{H-SiMe}_2\text{OSiMe}_2\text{Si-H} + \text{carbosilane}(CH_2CH{=}CH_2)_n \rightarrow \text{calix-dendrimers} \quad (1)$$

Scheme 1 outlines the synthesis of the calix[4]arene portion **5**, based largely on the work of Gutsche and co-workers.[21,22] The final step f involves hydrosilylation with TMDS of the functionalized monoallyl compound **5** to form the calix[4]arene attached to the linker (**6**). This synthesis may be modified to accommodate many calixarene types.

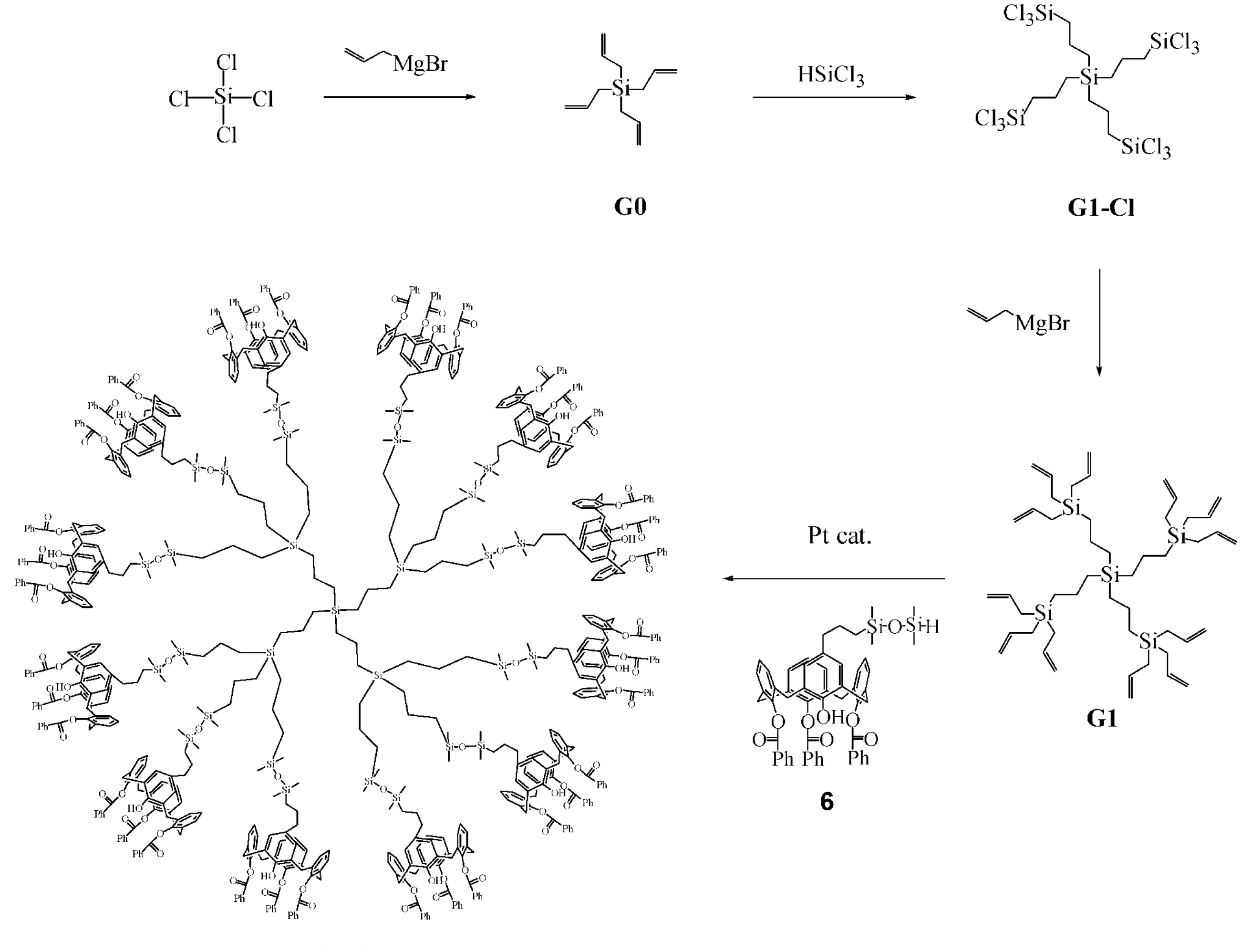
Reaction of tetrachlorosilane with 4 equiv of allylmagnesium bromide yielded the zeroth generation carbosilane (tetraallylsilane, **G0**) (Scheme 2). Hydrosilylation of **G0** with 4 mol of the linker-attached calix[4]arene **6** produced the zeroth generation carbosilane attached to four calix[4]arene units (Scheme 2), which we designate **G0-CX4**, for dendritic generation zero with four calix[4]arenes.

Hydrosilylation of tetraallylsilane (**G0**) with trichlorosilane gave the dodecachloro first generation dendrimer (**G1-Cl** in Scheme 3), which on reaction with 12 equiv of allylmagnesium bromide gave the first generation dodecaallyl carbosilane (**G1**). Hydrosilylation of **G1** with 12 mol of the linker-attached calix[4]arene **6** produced the first generation carbosilane attached to 12 calixarene units (Scheme 3), which we designate **G1-CX12**, for dendritic generation one with 12 calix[4]arenes.

This approach is easily adapted for higher generations. To achieve a second generation dendrimer (with 36 calixarene units), the compound **G1** in Scheme 3 would be hydrosilylated 12 times with $HSiCl_3$, and the resulting polychloride would be reacted with allylmagnesium bromide to give a 36-tipped polyallyl dendrimer. This second generation product could either be ligated with 36 calixarenes to complete the second generation synthesis or hydrosilylated 36 times with $HSiCl_3$ to begin the third generation synthesis.

Syntheses were optimized by identification of the byproducts and appropriate adjustment of conditions. In the conversion of the allyl compound **5** to the first hydrosilylation product **6** (Scheme 1), byproducts included double bond migration, hydrogenation, hydrolysis, and reaction with the solvent tet-

SCHEME 3



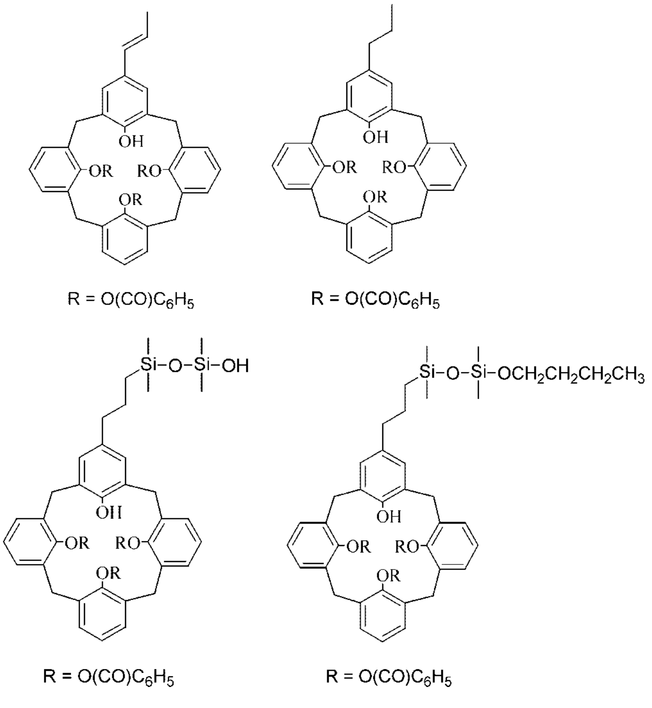
G1-CX12

rahydrofuran (Scheme 4). Other byproducts included the result of reaction of only three of the four allyl groups of **G0** in Scheme 2. All these byproducts could be recognized in the NMR spectra. The products of hydrolysis and hydrogenation could be reduced by using strictly anhydrous conditions. Reaction with solvent was reduced by using mixed dimethylformamide and tetrahydrofuran. Column chromatography was effective in purifying the desired product from the remaining byproducts to give a 61% isolated yield of **G0-CX4** and a 42% isolated yield of **G1-CX12**.

Characterization. Compounds **1**−**5** were known from the work of Gutsche and co-workers.[21,22] The dendrimers **G0-CX4** and **G1-CX12** were characterized by NMR spectroscopy, electrospray mass spectrometry, and elemental analysis (see the Experimental Section and the Supporting Information). All 236 protons in the first generation dendrimer and 732 protons in the second generation dendrimer were accounted for. The respective expected molecular weights of 3858 and 5888.5 were corroborated, and the elemental analyses were very accurate. Thus the molecules are well characterized in bulk.

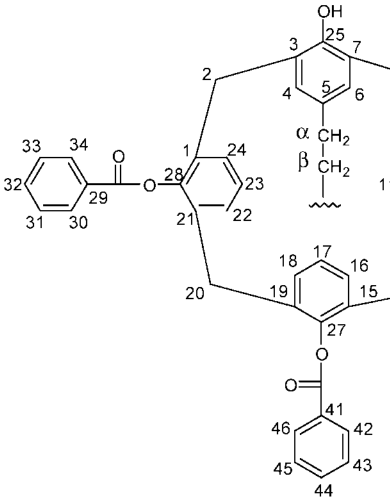
The conformations in solution of both **G0-CX4** and **G1-CX12** could be determined by examination of the Overhauser cross peaks in the NOESY spectra. The methylene group labeled α in the illustrated numbering scheme below showed a cross peak with the 4 and 6 protons but not with any of the protons on the other aromatic rings. The 2 and 8 methylene protons directed

SCHEME 4



downward (in the same direction as the α methylene group) exhibited cross peaks with the 4, 6, 10, and 24 aromatic protons, indicating that all three phenyl rings point in the same direction. The 14 and 20 methylene protons directed downward exhibited cross peaks with the 12 and 22 aromatic protons, but the 14 and 20 methylene protons directed upward had cross peaks with the 16 and 18 aromatic protons. These spectral observations are consistent with a partial cone (paco) conformation with the middle benzoyloxy-substituted aromatic ring directed to the opposite side of the cone from the other three aromatic rings. This assignment is based on the assumption that the downward-directed methylene protons are at lower frequency because of shielding by the faces of the adjacent aromatic rings.[23]

Numbering Scheme



Summary and Conclusions

We have prepared a new architecture of relatively immobilized calixarenes by attaching calix[4]arenes to dendritic carbosilanes. The largest previous branched system contained five calixarenes.[11,15,16] The only reported calixarene-terminated dendrimer is a heptacalixarene,[17] but various other end-group hosts have been examined.[24] The new family of hosts was prepared by ligating a polyallyl carbosilane with independently synthesized allyl-substituted calix[4]arene (Schemes 2 and 3). The ligating agent was 1,1,3,3-tetramethyldisiloxane, containing two Si−H groups. One Si−H hydrosilylates the allyl group on the derivatized calix[4]arene **5** and the other Si−H hydrosilylates the allyl groups on the polylallyl carbosilane (**G0** or **G1**). The zeroth order tetrabranched **G0-CX4**, prepared in two steps, contains four calix[4]arene units arranged via carbosilane linkers to a silicon core. The first generation dendritic **G1-CX12**, prepared in four steps, contains 12 calix[4]arene units connected via a 3-fold branching point to the 4-fold-substituted silicon core. Each additional generation would require two more synthetic steps.

The resulting dendrimers permit maximum accumulation of calixarene units because the interior is composed of the relatively unencumbered carboxilane units (previous branched and dendritic calixarenes used calixarenes as core and branching points as well as termini). Moreover, the interior carbosilane dendritic structure is not capable of binding, so that the terminal calixarenes are the only potential binding points in these molecules. The next stage of this program involves selection of the substituents on the calix[4]arene host **5** for optimal binding with metal cations.

Experimental Section

4-*tert*-Butylcalix[4]arene (**1**) was synthesized on a ca. 50 g scale in 49% yield by the method of Gutsche et al.[21]

25,26,27,28-Tetrahydroxylcalix[4]arene (**2**) was synthesized on a ca. 15 g scale in 75% yield by the method of Gutsche and Lin.[22]

25,26,27-Tris(benzoyloxy)-28-hydroxycalix[4]arene (**3**) was synthesized on a ca. 20 g scale in 78% yield by the method of Gutsche and Lin.[22]

25-(Allyloxy)-26,27,28-tris(benzoyloxy)calix[4]arene (**4**) was synthesized on a ca. 6 g scale in 42% yield by the method of Gutsche and Lin.[22]

5-Allyl-25-hydroxy-26,27,28-tris(benzoyloxy)calix[4]arene (**5**) was synthesized on a ca. 6 g scale in 77% yield by the method of Gutsche and Lin.[22]

5-[3-(1,1,3,3-Tetramethyldisiloxyl)propyl]-25-hydroxy-26,27,28-tris(benzoyloxy)calix[4]arene (6). Compound **5** (2.11 g, 0.0027 mol), dried THF (20 mL), TMDS (3.62 g, 0.0269 mol), and Karstedt's catalyst[25] (100 μL, 2.1−2.4% Pt in xylene) were placed in a 250-mL, two-necked, round-bottomed flask equipped with a condenser and a magnetic stirrer under N_2 atmosphere. The mixture was stirred at room temperature for 0.5 h and then warmed to 50 °C for 24 h. The solvent and excess TMDS were removed under vacuum. The residue was dried under the vacuum overnight to give 2.01 g (82%) of **6**: ^{1}H NMR (CDCl$_3$, 500 MHz) δ 8.07 (d, $J = 7.7$ Hz, 4H, H$_{30,34,36,40}$), 7.74 (t, $J = 7.3$ Hz, 2H, H$_{32,38}$), 7.56−7.52 (m, 5H, H$_{31,33,37,39,44}$), 7.28−7.22 (m, 4H, H$_{42,43,45,46}$), 7.03 (d, $J = 6.6$ Hz, 2H, H$_{10,24}$), 6.87 (d, $J = 6.6$ Hz, 2H, H$_{16,18}$), 6.81 (s, 2H, H$_{4,6}$), 6.70 (t, $J = 7.7$ Hz, 1H, H$_{17}$), 6.60−6.58 (m, 4H, H$_{11,12,22,23}$) 5.18 (s, 1H, OH), 4.68 (br s, 1H, SiH), 3.86 (d, $J = 15.1$ Hz, 2H, H$_{2,8\ \mathrm{up}}$), 3.82 (d, $J = 15.1$ Hz, 2H, H$_{14,20\ \mathrm{up}}$), 3.70 (d, $J = 15.1$ Hz, 2H, H$_{14,20\ \mathrm{down}}$), 3.50 (d, $J = 15.1$ Hz, 2H, H$_{2,8\ \mathrm{down}}$), 2.42 (t, $J = 7.4$ Hz, 2H, ArCH_2CH$_2$), 1.57−1.53 (m, 2H, ArCH$_2$CH_2), 0.53 (t, $J = 7.5$ Hz, 2H, CH$_2$Si), 0.18−0.04 (m, 12H, SiCH$_3$); ^{13}C NMR (CDCl$_3$) δ 0.4, 1.7, 18.3, 25.9, 33.2, 37.3, 38.9, 125.3, 126.2, 127.7, 128.0, 128.3, 128.9, 129.1, 129.4, 129.7, 130.5, 131.0, 131.6, 133.0, 133.0, 133.13, 133.4, 133.7, 133.9, 133.9, 147.0, 148.5, 151.0, 164.1, 164.5; ^{29}Si NMR (CDCl$_3$) δ 7.34, −11.65. Anal. Calcd. (found) for $C_{56}H_{54}O_8Si_2$: C, 73.82 (73.84); H, 5.97 (5.85).

Tetraallylsilane (**G0**) was synthesized on a ca. 25 g scale in 93% yield by the method of van der Made and van Leeuwen.[19]

First Generation Dodecaallyl Carbosilane (G1). Tetraallylsilane was hydrosilyated with $HSiCl_3$, and the product was allowed to react with 12 equiv of allylmagnesium bromide according to the method of van der Made and van Leeuwen[19] to produce **G1** on a scale of ca. 20 g in 90% yield: ^{29}Si NMR (CDCl$_3$) 0.66, −1.05. Anal. Calcd (found) for $C_{48}H_{84}Si_5$: C, 71.92 (72.09); H, 10.56 (10.65).

Dendritic Zeroth Generation Tetracalix[4]arene-End-Capped Carbosilane (G0-CX4). Compound **6** (1.80 g, 0.0020 mol), dried THF (30 mL), tetraallylsilane (**G0**, 0.04 g, 0.32 mmol), and

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Karstedt's catalyst[25] (20 μL, 2.1−2.4% Pt in xylene) were placed in a 50-mL, two-necked, round-bottomed flask equipped with a condenser and a magnetic stirrer under N_2 atmosphere. The mixture was stirred at room temperature for 15 min and then at 45 °C for 3 days. The flask was cooled, and the solvent was removed under vacuum to produce a light yellow solid. The mixture was purified by column chromatography over silica gel with ethyl acetate and hexane as the eluents (38:5) to give 0.76 g (61%) of **G0-CX4**: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.09 (d, J = 7.6 Hz, 16H, $H_{30,34,36,40}$), 7.74 (br s, 8H, $H_{32,38}$), 7.56−7.51 (m, 20H, $H_{31,33,37,39,44}$), 7.23 (br s, 16H, $H_{42,43,45,46}$), 7.03 (br s, 8H, $H_{10,24}$), 6.87 (d, J = 6.6 Hz, 8H, $H_{16,18}$), 6.81 (s, 8H, $H_{4,6}$), 6.71 (t, J = 7.6 Hz, 4H, H_{17}), 6.60−6.58 (m, 16H, $H_{11,12,22,23}$) 5.18 (s, 4H, OH), 3.86 (d, J = 15.1 Hz, 8H, $H_{2,8\ \mathrm{up}}$), 3.85 (d, J = 15.1 Hz, 8H, $H_{14,20\ \mathrm{up}}$), 3.72 (d, J = 15.1 Hz, 8H, $H_{14,20\ \mathrm{down}}$), 3.50 (d, J = 15.1 Hz, 8H, $H_{2,8\ \mathrm{down}}$), 2.44 (br s, 8H, ArCH_2CH_2), 1.54 (br s, 8H, $ArCH_2CH_2CH_2$), 1.47 (br s, 8H, $SiCH_2CH_2CH_2Si$), 0.61−0.58 (m, 16H, $SiCH_2$), 0.52 (br s, 8H, $SiCH_2$), 0.07 (s, 24H, $SiCH_3$), 0.03 (s, 24H, $SiCH_3$); ^{13}C NMR ($CDCl_3$) δ 0.8, 18.4, 26.0, 33.1, 37.7, 39.0, 125.4, 126.2, 127.8, 128.0, 129.0, 128.9, 129.1, 129.4, 129.8, 130.5, 131.1, 131.6, 133.0, 133.2, 133.4, 133.7, 134.0, 147.1, 148.5, 151.0, 164.2, 164.7; ^{29}Si NMR ($CDCl_3$) δ 7.47, 6.75, −3.33; MS (MALDI-TOF) *m/z* calcd (found) for $(C_{236}H_{236}O_{32}Si_9 + Na)^+$ 3858 (3858.7). Anal. Calcd (found) for $C_{236}H_{236}O_{32}Si_9$: C, 73.87 (73.34); H, 6.20 (6.23).

Dendritic First Generation Dodecacalix[4]arene-End-Capped Carbosilane (G1-CX12). Compound **6** (2.14 g, 0.24 mol), dried THF (30 mL), the first generation, dodecaallyl carbosilane (**G1**, 0.13 g, 0.17 mmol), and Karstedt's catalyst[25] (20 μL, 2.1−2.4% Pt in xylene) were placed in a 50-mL, two-necked, round-bottomed flask equipped with a condenser and a magnetic stirrer under N_2 atmosphere. The mixture was stirred at room temperature for 15 min and at reflux for 4 days. The flask was cooled, and the solvent was removed under vacuum to yield a light yellow solid. The mixture was purified initially through a silica gel column with CH_2Cl_2 and hexane as the eluent (7:1) and then through silica gel with ethyl acetate, hexane, and CH_2Cl_2 (4:2:4) to give 0.83 g (42%) of **G1-CX12**: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.06 (d, J = 7.6 Hz, 48H, $H_{30,34,36,40}$), 7.74 (br s, 24H, $H_{32,38}$), 7.48 (br s, 60H, $H_{31,33,37,39,44}$), 7.25 (br s, 24H, $H_{43,46}$), 7.22 (br s, 24H, $H_{42,45}$), 7.03 (br s, 24H, $H_{10,24}$), 6.86 (d, J = 6.5 Hz, 24H, $H_{16,18}$), 6.80 (s, 24H, $H_{4,6}$), 6.71 (t, J = 7.6 Hz, 12H, H_{17}), 6.59 (br s, 48H, $H_{11,12,22,23}$) 5.18 (s, 12H, OH), 3.84 (d, J = 14.8 Hz, 24H, $H_{2,8\ \mathrm{up}}$), 3.81 (d, J = 14.8 Hz, 24H, $H_{14,20\ \mathrm{up}}$), 3.70 (d, J = 14.8 Hz, 24H, $H_{14,20\ \mathrm{down}}$), 3.42 (d, J = 14.8 Hz, 24H, $H_{2,8\ \mathrm{down}}$), 2.42 (br s, 24H, $ArCH_2CH_2$), 1.52 (br s, 24H, $SiCH_2CH_2$), 1.33 (br s, 24H, $SiCH_2CH_2$), 1.24 (s, 18H, $SiCH_2CH_2$), 0.58 (br s, 54H, $SiCH_2$), 0.52 (br s, 24H, $SiCH_2$), 0.09 (s, 72H, $SiCH_3$), 0.02 (s, 72H, $SiCH_3$); ^{13}C NMR ($CDCl_3$) δ 0.8, 18.5, 26.0, 33.1, 37.7, 39.0, 125.4, 126.0, 127.8, 128.0, 128.4, 128.9, 129.1, 129.4, 129.8, 130.6, 131.0, 131.6, 133.1, 133.2, 133.5, 133.7, 134.0, 147.1, 148.55, 151.1, 164.2, 164.7; ^{29}Si NMR ($CDCl_3$) δ 7.37, 6.76, 0.92, −3.99; MS (MALDI-TOF) *m/z* calcd (found) for $(C_{720}H_{732}O_{96}Si_{29} + 2Na)^{2+}$ 5888.5 (5888.5). Anal. Calcd (found) for $C_{720}H_{732}O_{96}Si_{29}$: C, 73.69 (73.76); H, 6.29 (6.19).

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Supporting Information Available: ^{1}H spectra of **2**−**6**, **G0**, **G0-CX4**, **G1**, and **G1-CX12**, ^{13}C spectra of **6**, **G0-CX4**, and **G1-CX12**, and ^{29}Si spectra of **6**, **G0-CX4**, and **G1-CX12**. This material is available free of charge via the Internet at http://pubs.acs.org.

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