

End-Capped Silole Dendrimers on a Carbosilane Periphery: Potential Electroluminescent Materials[†]

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The divergent synthesis of end-capped silole dendrimers **Gn-2ⁿ⁺¹Silole** ($n = 1-4$) using 2,4,6,8-tetramethyl-2,4,6,8-tetravinylcyclotetrasiloxane [Me(CH₂=CH)SiO]₄ as a core molecule and allyl alcohol/dichloromethylsilane as a building block is described in this paper. The reaction of the dichloride functionalities of the carbosiloxane dendrimers **Gn-2ⁿ⁺²Cl** ($n = 1-4$) with the 1,4-diphenylbutadiene-1,4-dianions (**1**) provided an effective route for the attachment of silole functionalities to a dendritic periphery. In addition, dendritic siloles **GBn-2ⁿSilole** ($n = 1-3$) based on phenylethynylmethylsilane (PhC≡C)₂Me₂Si as cores were synthesized. The building blocks of the dendrimers consisted of double bonds (–PhC≡CHMeSi–) in the inner shell and silole groups on the outermost periphery. The generational limit of the dendrimer for the two-branching type core molecule was found to have eight silole groups for the third generation. All of the dendrimers were characterized by ¹H and ¹³C{¹H} NMR, UV spectroscopy, cyclic voltammetry (CV), and size exclusion chromatography (SEC). Using this methodology, a series of silole-containing dendrimer systems showing green to greenish-blue fluorescence were synthesized.

Introduction

Dendritic macromolecules containing π -conjugated systems have attracted a great deal of attention owing to their potential to act as photosynthetic antennas¹ and molecular wires for electron and energy transfer² and also to their potential applications in organic photo- and electroluminescent devices.³ The majority of electroluminescent dendrimers reported to date have been prepared using dendrons or cores with chromophoric centers.^{4,3b,d} Although chromophore-functionalized dendrimers have received much attention,⁵ dendrimers adorned with silole derivatives have yet to be reported. Our interest in the potential

of silole derivatives to act as new types of chromophores led us to prepare a dendrimeric version of this chromophore and to explore its behavior. Silole and its derivatives, especially the 2,3,4,5-tetraphenylsilacyclopentadienes, are well known for their versatility in emitting⁶ and electron-transporting (ET) materials⁷ for light-emitting devices (LEDs). The advantageous properties of the silole unit, most notably a high fluorescent quantum yield,^{6c,8} photostability, and chemical stability,⁹ thus served as the primary motivation for our work in implementing dendrimeric versions of this silole. In addition, the peripheral dichlo-

[†] Dedicated to Prof. Larry G. Sneddon on the occasion of his 60th birthday.

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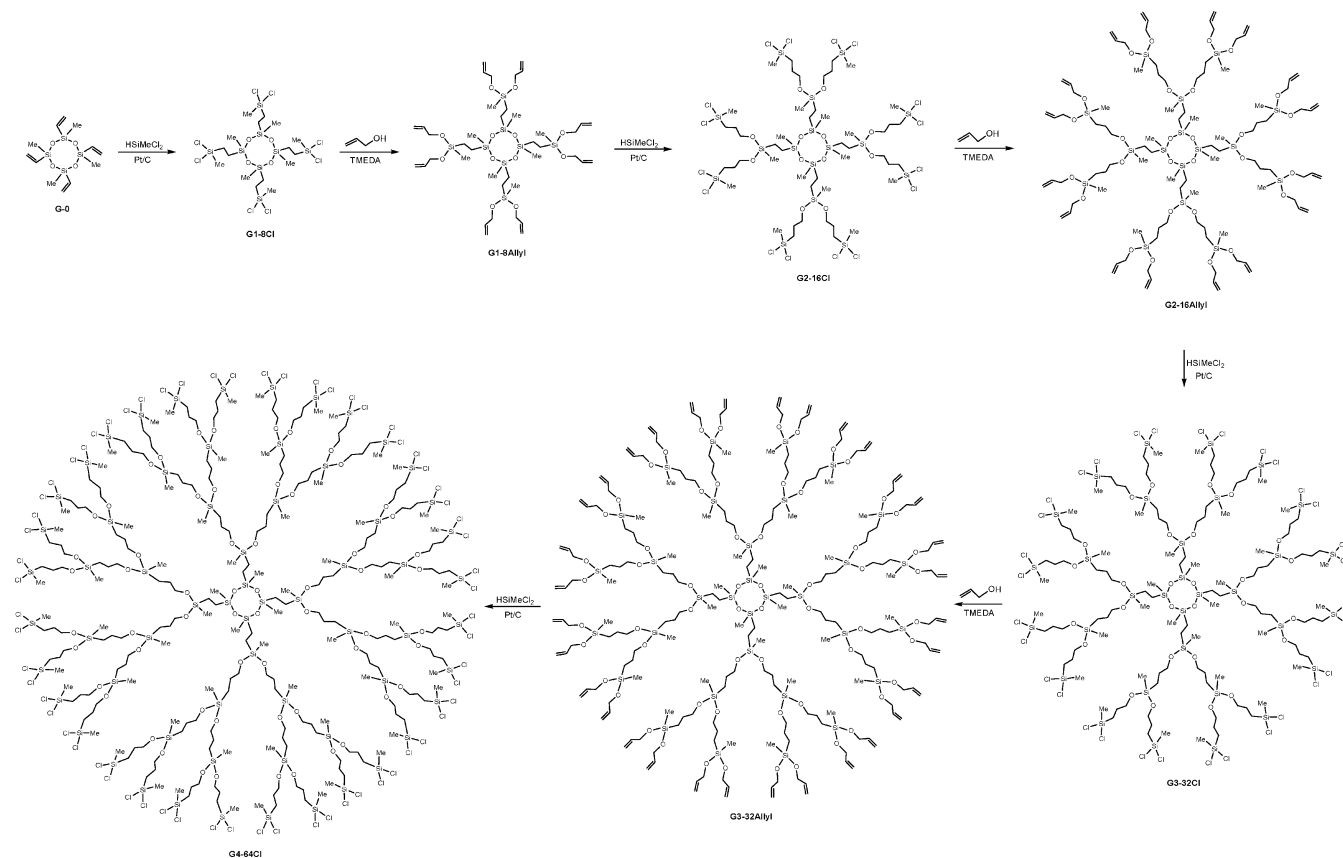
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Scheme 1. Preparation of G_n-2^{n+2} Allyl and G_n-2^{n+2} Cl

rosilane unit in carbosiloxane and carbosilane dendrimers¹⁰ is recognized as a useful core unit due to its versatile and well-established chemistry, which permits the preparation of a wide range of molecular structures. Thus, reaction of the peripheral dichlorosilane unit is an ideal method for capping the well-known carbosiloxane and carbosilane dendrimers of silole groups, provided that suitable dichlorosilane-functionalized dendrimers can be prepared.¹¹ With these considerations in mind, we prepared low-generation dendrimers with peripheral silole units using the appropriate carbosiloxane and carbosilane dendrimer framework, as well as the lithium 1,3-diyne, **1**.

Results and Discussion

As an extension of our recent research in the molecular architecture of carbosilane dendrimers with unique functional groups on the periphery,¹² the synthesis and identification of the end-capped dendrimers with siloles are reported in this paper. Dendritic scaffolds with terminal SiCl_2 units were synthesized by successive hydrosilylation–alcoholysis steps starting with $[\text{Me}(\text{CH}_2=\text{CH})\text{SiO}]_4$ as the core molecule.^{10b,13} Thus, the parent dendrimers were constructed with a siloxane tetramer $[\text{MeSi}$

$(\text{CH}=\text{CH}_2\text{O})_4$ as the core and allyloxysilyl groups $-\text{SiMe}(\text{OCH}_2\text{CH}=\text{CH}_2)_2$ as generating units, as shown in Scheme 1.

The hydrosilylation reaction of **G0** with dichloromethylsilane in the presence of a platinum catalyst produced **G1-8Cl**. The first generation **G1-8Allyl** with eight allyloxy groups on the peripheral layer was obtained through a reaction of **G1-8Cl** with allyl alcohol in the presence of TMEDA. The second hydrosilylation reaction of **G1-8Allyl** with dichloromethylsilane produced **G2-16Cl**. Subsequent alcoholysis of **G2-16Cl** with allyl alcohol produced the **G2-16Allyl** dendrimer, which was obtained in a pure form with a good yield after simple column chromatography with toluene. Using repetitive hydrosilylation of G_n-2^{n+2} Allyl ($n = 0-4$) with dichloromethylsilane and allyl alcohol-based alcoholysis, dendrimers adorned with 64 dichloromethylsilyl groups on their periphery were prepared up to the fourth generation in good yields. It has been noted that, during the hydrosilylation procedure of G_n-2^{n+2} Allyl, two different branches were formed in one molecule. There is no doubt that the major products were hydrosilylated branches. As minor products, dehydrogenatively coupled branches were found (see Supporting Information). This result indicated that the hydrosilylation process and dehydrogenative coupling process occurred simultaneously in the stated condition. In contrast to the previous hydrosilylation of vinyl-terminated dendrimers with $\text{HSiMe}_2\text{CH}_2\text{Cl}$,¹⁴ only one form of regioisomer, namely, β -added branches, was found. Thus, the β -added branches ($-\text{OCH}_2\text{CH}_2-\text{CH}_2\text{SiMeCl}_2$) predominated, but dehydrogenatively coupled branches ($-\text{OCH}_2\text{CH}=\text{CHSiMeCl}_2$) were detected in the ¹³C NMR spectra of the crude product mixtures (in amounts of less

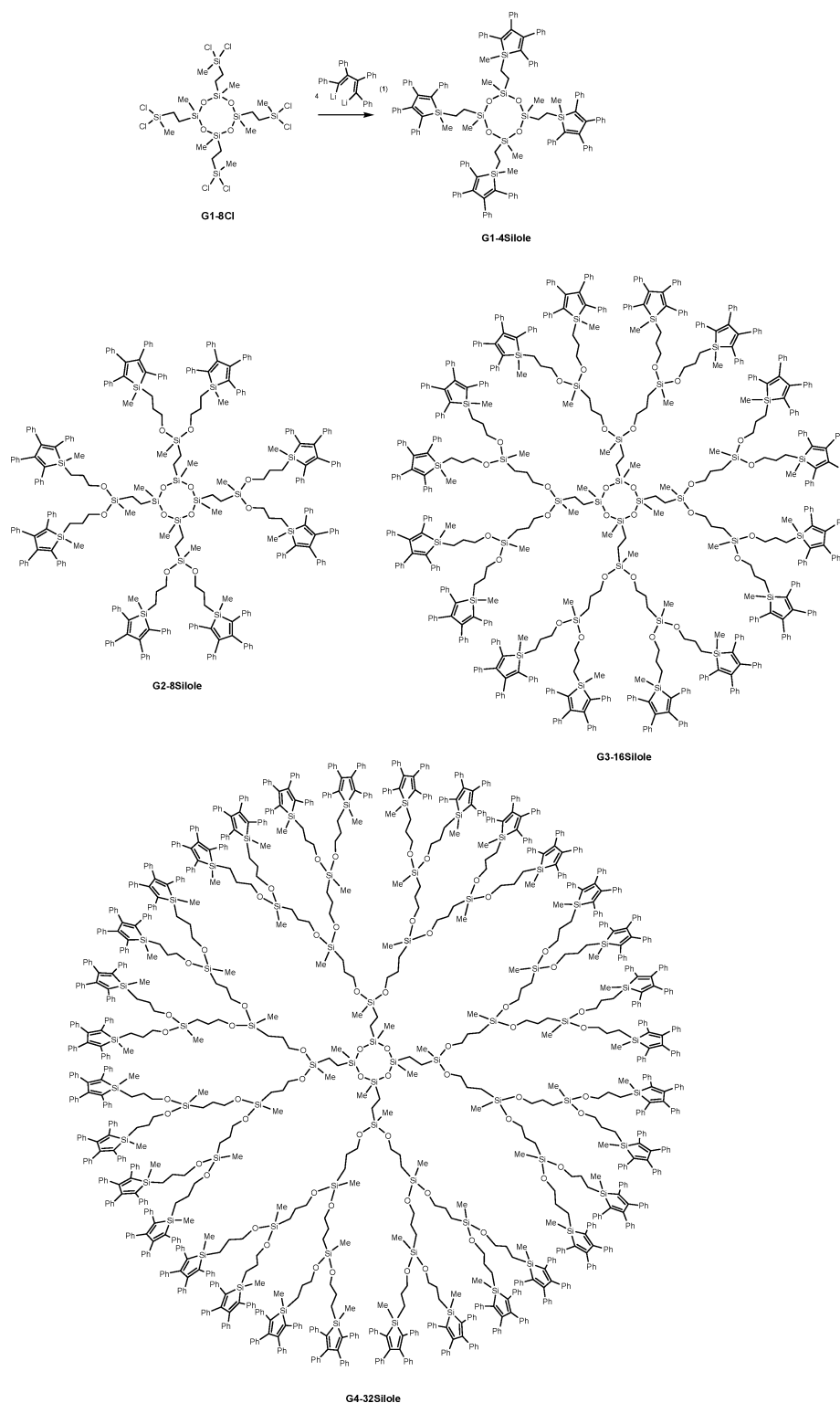
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Scheme 2. Preparation of $Gn-2^{n+1}$ Silole

than 5%) by the observation of characteristic peaks at 105.46 and 137.66 ppm.^{13c} However, certain reaction conditions, such as reaction temperature and medium, were adjusted to minimize the number of branches resulting from dehydrogenative coupling. Thus, the use of a low reaction temperature and polar solvent effectively suppressed the production of dehydrogenatively coupled branches. The purification of G_n type dendrimers was carried out by chromatography after each alcoholysis step. The purification of $G_n-2^{n+2}Cl$ type dendrimers was not possible due to their sensitivity to moisture. But, the NMR spectroscopic data confirmed a perfect formation of all generations.

Silole end-capped dendrimers ($G_n-2^{n+1}Silole$) of the first to fourth generation were successfully prepared through a direct reaction of the 1,4-diphenylbutadiene-1,4-dianions (1) with $SiCl_2$ -terminated carbosiloxane dendrimers $G_n-2^{n+2}Cl$. To illustrate these results, the synthesis of the first-generation end-capped silole dendrimer and a simplified drawing of each dendrimer are shown in Scheme 2.

Thus, the reaction of G_4-64Cl with 1 produced the $G_4-32Silole$ in good yields. The light yellow colored $G_4-32Silole$ was obtained as a pure form after simple column chromatography with benzene/hexane. The $G_4-32Silole$ had three propyl-

Table 1. Selected ^1H and ^{13}C NMR Spectroscopic Data of $\text{Gn-2}^{n+1}\text{Silole}$ and $\text{GBn-2}^n\text{Silole}$

compound		SiCH_3	$-\text{CH}_2-$	$-\text{OCH}_2-$	compound	SiCH_3	$\text{CH}=\text{C}$	
G1-4Silole	^1H	-0.14 (s, 12H, G0) 0.39 (s, 12H, G1)	0.83–0.88 (m, 16H, G0)		GB1-2Silole	^1H	-0.45 (s, 6H, G0) 0.59 (s, 6H, G1)	6.50 (s, 2H, G0)
	^{13}C	-5.76 (G0), -1.43 (G1)	4.59, 8.62 (G0)			^{13}C	-6.94 (G1), -0.46 (G0)	148.64, 155.78 (G0)
G2-8Silole	^1H	-0.053 (m, 24H, G0-G1) 0.43 (m, 24H, G2)	0.81–1.03, 1.42–1.63 (m, 48H, G0-G1)	3.38–3.61 (m, 16H, G1)	GB2-4Silole	^1H	-0.77 (s, 6H, G0) -0.59 (s, 6H, G1)	5.65 (s, 2H, G0) 6.40 (s, 4H, G1)
	^{13}C	-1.46 (G0), -5.77 (G1) -5.47 (G2)	4.83, 8.72 (G0) 9.09, 26.54 (G1)	64.77 (G1)		^{13}C	0.51 (s, 12H, G2) -0.30 (G0), -3.01 (G1) -6.96 (G2)	145.36, 163.18 (G0) 146.00, 160.89 (G1)
G3-16Silole	^1H	0.04 (m, 48H, G0-G2) 0.44 (s, 48H, G3)	0.88–0.99, 1.40–1.71 (m, 112H, G0-G2)	3.39–3.63 (m, 48H, G1-G2)	GB3-8Silole	^1H	-0.76 (s, 6H, G0) -0.48 (s, 6H, G1) -0.89 (s, 12H, G2) 0.50 (s, 24H, G3)	5.98 (s, 2H, G0) 6.37 (s, 4H, G1) 6.40 (s, 8H, G2)
	^{13}C	-1.82 (G0), -5.62 (G1) -4.87 (G2), -5.44 (G3)	4.98, 8.72 (G0) 9.59, 26.02 (G1) 9.11, 26.56 (G2)	64.76 (G1-G2)		^{13}C	0.23 (G0), -2.97 (G1) -3.19 (G2), -6.91 (G3)	146.23, 163.45 (G0) 146.10, 163.24 (G1) 145.42, 162.45 (G2)
G4-32Silole	^1H	0.01 (m, 96H, G0-G3) 0.43 (s, 96H, G4)	0.79–1.03, 1.39–1.70 (m, 240H, G0-G3)	3.51 (m, 112H, G1-G3)				
	^{13}C	-1.82 (G0), -1.79 (G1) -5.54 (G2), -4.87 (G3) -5.44 (G4)	4.98, 8.60 (G0) 10.89, 22.45 (G1) 9.25, 26.03 (G2) 9.12, 26.56 (G3)	64.75 (G1-G3)				

eneoxy layers in the inner shell and 32 silole groups on the periphery. Low-generation silole dendrimers, such as the **G1-4**, **G2-8**, and **G3-16Siloles**, were produced by employing the same preparative synthetic method used for the **G4-32Silole**. In all cases the terminal dichlorosilyl groups reacted completely with the dilithium salt of a diyne (**1**) to give dendrimers with monodisperse GPC traces and no residual dichloromethylsilyl resonances in their ^1H NMR spectra. The first-generation dendrimers were green-colored solids, but the second- through fourth-generation dendrimers were hard gels. All generations exhibited a ready solubility in a wide range of solvents, including toluene, CH_2Cl_2 , Et_2O , and THF.

The identification of the $\text{Gn-2}^{n+1}\text{Silole}$ was carried out using NMR spectroscopy (Table 1), size exclusion chromatography (SEC), UV spectroscopy, CV, and elemental analysis. The MALDI-TOF mass spectrum of the first generation showed molecular ion peaks (m/z) that agreed very closely with calculated values. However, mass spectra of higher generation dendrimers (**G2–G4**) did not show the fragmentations of the given compounds, implying that the products are not stable enough in this mass-measuring condition. Similar difficulties in obtaining mass spectroscopic data have frequently been encountered in the analysis of carbosiloxane dendrimers.¹⁵

Purity of the end-capped dendrimers was determined by SEC. The GPC data for each of the prepared end-capped dendrimers provided additional information for the unified character of all generations. The PDI values remained almost unchanged from the first to the fourth generation ($M_w/M_n = 1.004\text{--}1.016$). Therefore, the GPC measurement of the silole dendrimers

Table 2. GPC and UV Spectroscopic Data

compound	M_w	PDI	t_R (min)	UV spectroscopic data	
				λ_{max} (nm)	$\epsilon_{\text{max}} \times 10^4$ ($\text{M}^{-1} \text{cm}^{-1}$)
G1-4Silole	1947.00	1.004	18.32	230	0.16
G2-8Silole	4182.43	1.006	17.11	231	0.27
G3-16Silole	8653.28	1.016	16.65	229	0.43
G4-32Silole	17594.99	1.011	16.43	230	0.84
GB1-2Silole	1061.43	1.013	19.45	238	0.27
GB2-4Silole	2355.51	1.005	17.99	238	0.52
GB3-8Silole	4943.37	1.007	17.04	237	0.84

showed the pure dendritic properties that have very low polydispersity values (PDI) and regular retention time (Table 2). The difference between the theoretical and experimental molecular weights (relative to polystyrene standards) was due to the difference between the hydrodynamic volumes of polystyrene as a standard and the prepared monodendrons.

It has been noted that the molar absorptivities (ϵ_{max}) of $\text{Gn-2}^{n+1}\text{Silole}$ type dendrimers are proportional to the increasing number of silole groups in UV spectroscopy.¹⁶ In fact, the UV spectra of $\text{Gn-2}^{n+1}\text{Silole}$ are similar and consist of a broad band with a maximum wavelength (λ_{max}) at 229–231 nm. The molar absorptivities (ϵ_{max}) of all silole-capped dendrimers are approximately increasing according to the number of peripheral siloles (see Table 2). This shows that there are no unusual effects and that the silole end groups contribute to the UV absorption in an additive manner.

Similar proportionality of dendrimer growth was observed in the cyclic voltammograms. Each generation exhibited at least

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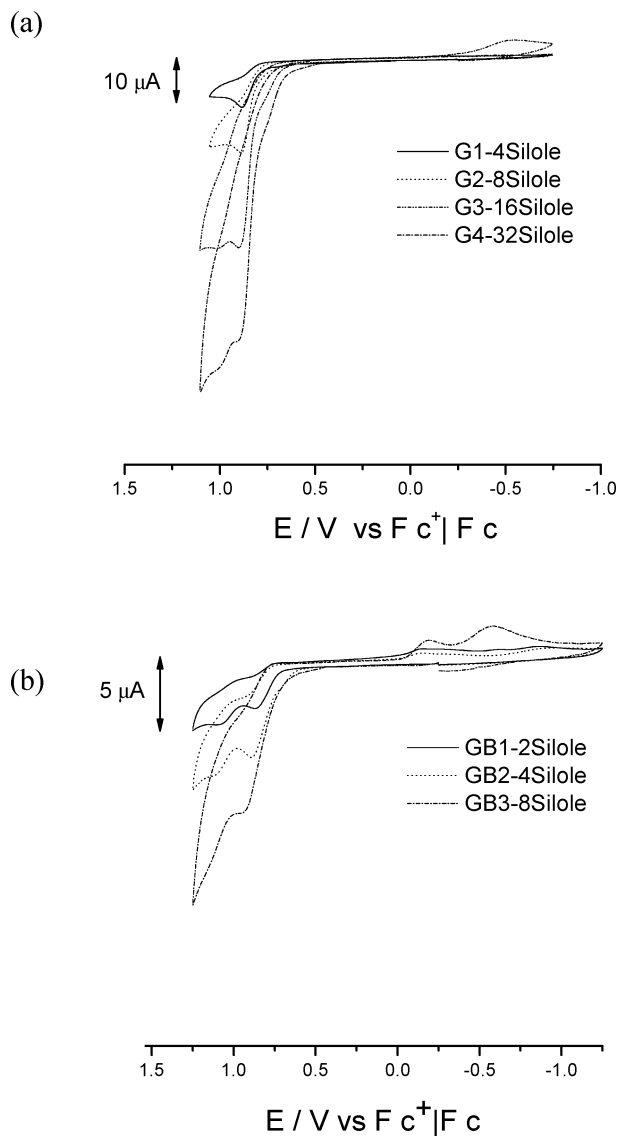


Figure 1. Cyclic voltammograms of (a) **G1-4Silole**, **G2-8Silole**, **G3-16Silole**, and **G4-32Silole** and (b) **GB1-2Silole**, **GB2-4Silole**, and **GB3-8Silole**.

one irreversible reduction wave and two irreversible oxidation waves. In particular, the peak current of the oxidative wave was proportional to the number of peripheral silole groups (see Figure 1). Therefore, the end-capped dendritic macromolecules from the **G1-4Silole** to the **G4-32Silole** generation were estimated to structural perfection.

Molecular modeling of the fourth generation (Figure 2) revealed an energetically stable disklike structure. Calculations showed that the effective thickness (1.4 nm) of the peripheral area was higher for the fourth generation as compared to the first generation, thus forming dense packing on the periphery.

Another series of end-capped silole dendrimers **GBn-2ⁿSilole**, containing alternating carbosilane-ethynyl core units, was prepared by reacting the dilithium salt of a diyne (**1**) with the corresponding SiCl_2 entity. Thus, **GBn-2ⁿ⁺¹Cl** ($n = 1-3$) were used to produce the corresponding end-capped silole dendrimers, as shown in Scheme 3. The formation of inner-shell branches with dichlorosilyl-terminated dendrimers **GBn-2ⁿ⁺¹Cl** was achieved through repeated iterations of alkylation and hydrosilylation on the dendritic surface.¹⁷

Dendritic carbosilanes with less sterically hindered models were prepared using two ethynyl branching groups as the core.

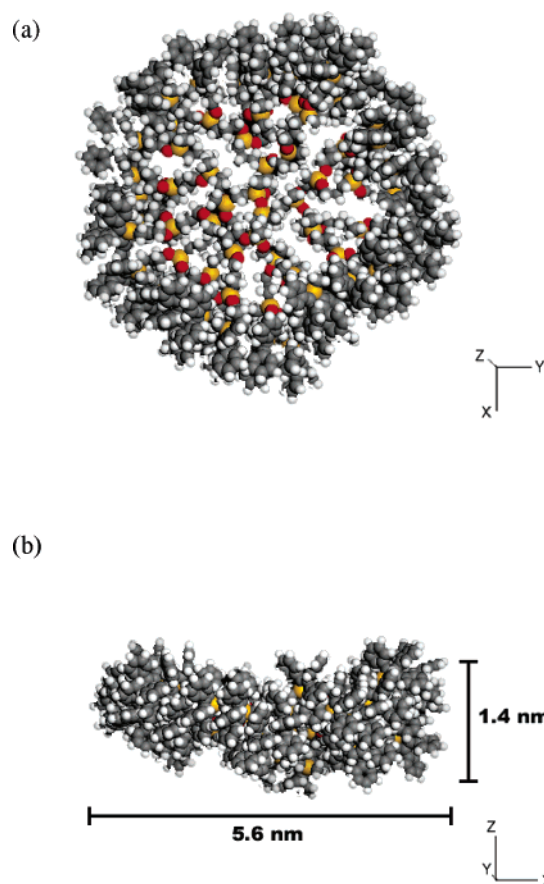


Figure 2. Molecular models of the fourth generation **G4-32Silole** as seen (a) from above and (b) from the side.

The hydrosilylation of the two-branched core $(\text{PhC}\equiv\text{C})_2\text{MeSi}$ (**GB0**) with excess dichloromethylsilane provided SiCl_2 bonds in terminal groups that facilitated the formation of the desired silole dendron. Platinum metal (Pt/C, 10% Pt content in activated carbon) was found to be a very useful catalyst for the preparation of carbosilane dendrimers. Indeed, a simple filtration of the reaction medium resulted in the quantitative formation of **GBn-2ⁿ⁺¹Cl** type dendrimers. Moreover, double-hydrosilylated or α -hydrosilylated dendritic branches were not observed in this case. The NMR spectroscopy revealed clearly the construction of new generations (see Supporting Information). For example, the transition from **GB0-2Ethyne** to **GB1-4Cl** can be easily obtained by observing the ^1H NMR spectrum. The ethynyl hydrogen ($-\text{CH}=\text{CPh}-$) and dichloromethylsilyl groups ($-\text{SiMeCl}_2$) were observed at 6.76 and 0.94 ppm, respectively. In addition, ^{13}C NMR revealed a chemical shift change from triple bonds at 90.67 and 105.92 ppm to double bonds at 149.47 and 157.08 ppm (see Supporting Information). In the next generation **GB2-8Cl**, the ethynyl hydrogen signals were observed at 6.49 and 6.06 ppm with a 2 to 1 intensity ratio. A similar peak pattern for the ethynyl hydrogens was observed in all generations of **GBn** type dendrimers, even though the ethynyl protons of each generation were present in different positions in the ^1H NMR spectra. The methyl signals of **GB1-4Cl** and **GB1-4Ethyne** were found at 0.94 and 0.40 ppm, respectively. Hence, NMR spectroscopy was shown to be a very useful tool in understanding the structural perfection of dendrimer preparations.

Among the ethynyl dendrimers produced, the structure of **GB1-4Ethyne** was determined using X-ray crystallography, as shown in Figure 3. This structural study corroborated well

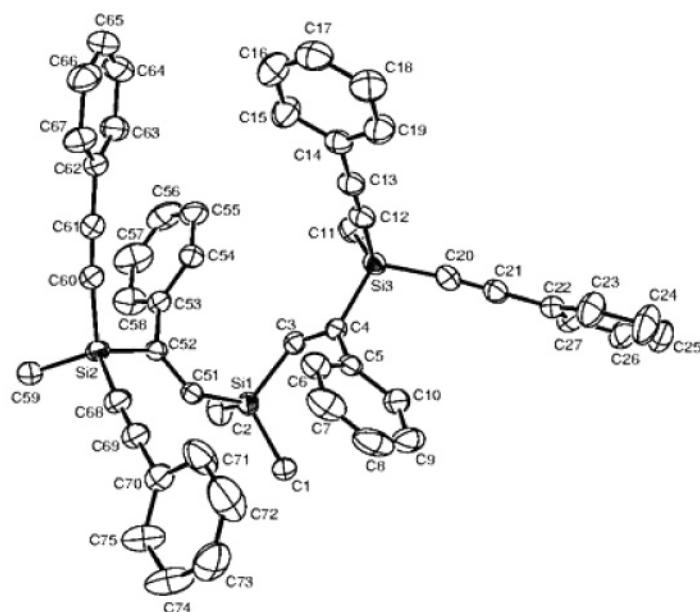
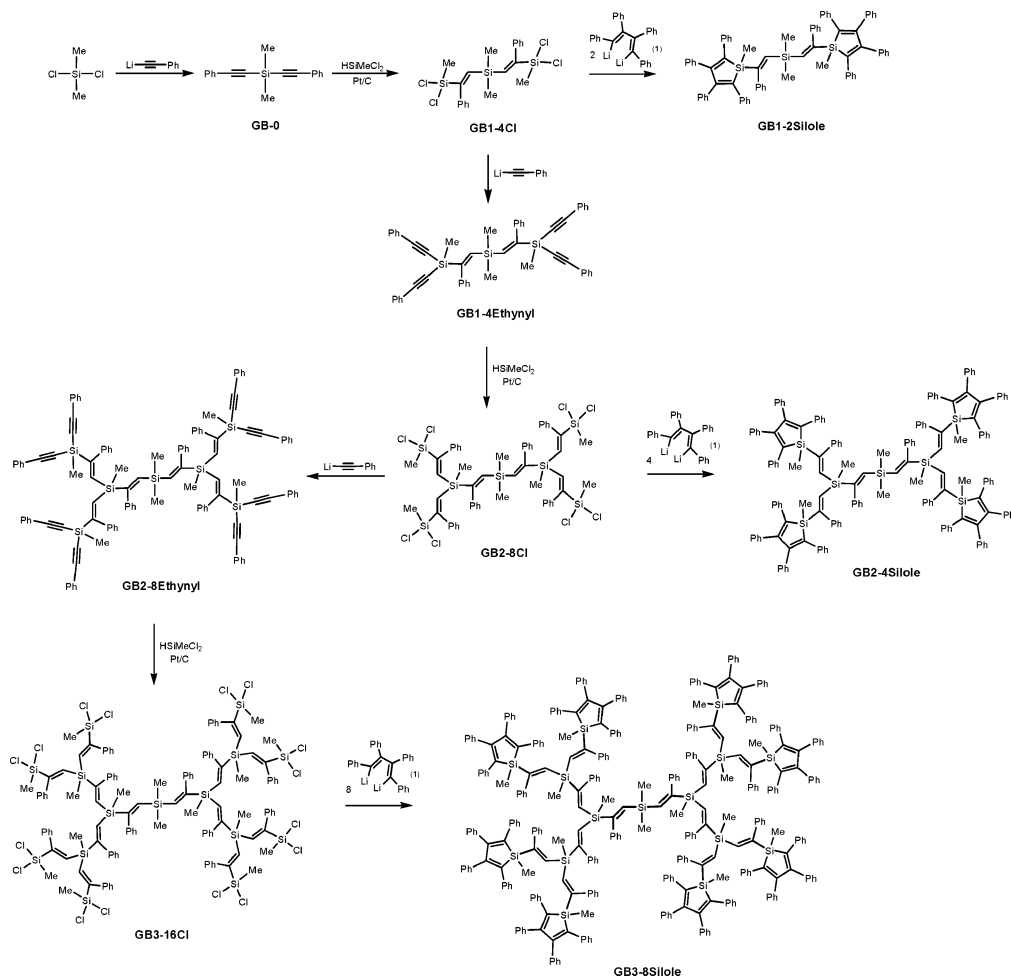


Figure 3. Molecular structure of **GB1-4Ethyneyl** with thermal ellipsoids drawn at the 30% level.

Scheme 3. Preparation of $\text{GBn-2}^n\text{Ethyneyl}$, $\text{GBn-2}^{n+1}\text{Cl}$, and $\text{GBn-2}^n\text{Silole}$



with the NMR data, authenticating the β -added conformation of the dendrimers resulting from the hydrosilylation process of phenylethyne units with MeSiHCl_2 . In addition, the structural study indicated that the conformation of the resulting dendrimers could be dependent on the core structure of their lower generation dendrimers due to the rigid nature of ethynyl-phenyl repeating units.

By applying the iterative hydrosilylation and alkylation procedure, the rigid dendritic synthons of the type $\text{GBn-2}^{n+1}\text{Cl}$ were produced almost quantitatively. The subsequent production of the silole dendrimers up to the third-generation **GBn-2ⁿSilole** was achieved from the reaction of $\text{GBn-2}^{n+1}\text{Cl}$ with the 1,4-diphenylbutadiene 1,4-dianions (**1**) at reflux conditions. Similar to $\text{Gn-2}^{n+1}\text{Silole}$, the **GBn-2ⁿSilole** showed good stability

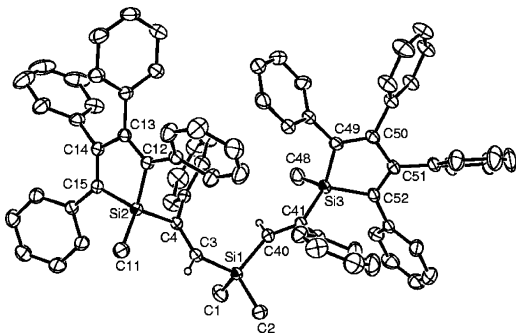


Figure 4. Molecular structure of **GB1-2Silole** with thermal ellipsoids drawn at the 30% level.

against air and moisture. Therefore, after metathesis, handling of the prepared dendrimers in the atmosphere became feasible. Thus, **GBn-2ⁿSilole** dendrimers can be obtained in pure form after simple column chromatography. However, due to the strained nature of the inner ethenyl backbone, peripheral silole formation was only achieved up to the third generation, i.e., **GB3-8Silole**. With the metathesis procedure, the **GB4-32Cl** dendrimer did not progress into a **GB4-16Silole** dendritic macromolecule. Therefore, the third generation with eight silole groups having a unified form on the periphery was found to be the limit for this particular model.

Among the new silole dendrimer systems produced, only the structure of the first generation **GB1-2Silole** was determined by X-ray crystallography, as shown in Figure 4. In the structure of the disilole **GB1-2Silole**, the two silole rings were arranged in *anti*-conformations along with the central C=C–SiMe₂ unit, having dihedral angles of 3.41(0.46)° and 5.08(0.10)° for Si(1)–C(3)–C(4)–Si(2) and Si(1)–C(40)–C(41)–Si(3), respectively. In this structure, there was a centrosymmetric point at the central silicon atom Si(1). The two bulky silole groups took up the least hindered positions, well-separated by the central silicon atom. All the bond lengths and angles in each silole ring were within normal parameters.^{7a,18} The structure of **GB1-2Silole** resembled that of **GB1-4Ethenyl** such that the gross conformation of each dendrimer depended on the rigid phenylethenyl core units.

The MALDI-TOF mass spectroscopic determination of **GBn-2ⁿSilole** dendrimers mainly showed a signal that was clearly due to the structural perfection of the prepared dendrimers. The *m/z* value of the **GB1-2Silole** showing a dominant signal at 1084.23 amu corresponds to the calculated value 1061.60 plus 23 for the Na⁺ ion. Both **GB2-4Silole** and **GB3-8Silole** were observed at 2377.02 (**GB2-4Silole**, calcd 2355.51 plus 23 for Na⁺ ion) and 4981.72 (**GB3-8Silole**, calcd 4943.37 plus 39 for K⁺) amu, respectively. Size exclusion chromatography provided additional information on the perfect building of each generation. The SEC-analyzed polydispersity value (*M_w/M_n*) for the dendrimers **GB1-2Silole** (1.013), **GB2-4Silole** (1.005), and **GB3-8Silole** (1.007) revealed that the prepared dendrimers had a very narrow molecular weight range (Table 2). In addition, a stepwise progression of dendrimer generation was monitored using cyclic voltammograms, in which the peak current was proportional to the number of peripheral silole groups (see Figure 1).

All of the silole dendrimers produced showed greenish-blue photoluminescence (Table 3). The siloxane dendrimers **Gn-2ⁿ⁺¹Silole** exhibited absorption maxima at 345–360 nm and emission maxima at 468–476 nm, whereas the absorption and

Table 3. Absorption and Emission Characteristics of **Gn-2ⁿ⁺¹Silole** and **GBn-2ⁿSilole**

compound	UV–vis λ_{\max} (nm)		PL λ_{\max} (nm)	
	solution ^a	film ^b	solution ^a	film ^b
G1-4Silole	230, 358	233, 361	476	483
G2-8Silole	231, 360	230, 359	476	482
G3-16Silole	229, 351	231, 353	468	479
G4-32Silole	230, 345	240, 354	476	480
GB1-2Silole	238, 369	238, 369	481	492
GB2-4Silole	238, 364	239, 375	474	483
GB3-8Silole	237, 367	240, 375	481	483

^a In chloroform solution. ^b Spin-coated thin film with a 100 nm thickness.

emission maxima of the carbosilane dendrimers **GBn-2ⁿSilole** were at slightly longer wavelengths. These values were similar to those observed for the monomeric 1,1'-dimethyl-silole, Ph₄C₄-SiMe₂.¹⁹

The electronic properties of siloles are intimately linked to the environment surrounding the silicon atom and to the nature of any coordinated substituents.^{19,20} As suggested by the crystallographic data for the **GB1-2Silole**, the silole groups in the dendrimer systems studied were confined in a well-separated unified environment by a central silene unit. This feature suggests that the differences in size and length of the macromolecular systems do not affect the silole microenvironment. An even more interesting finding is that the absorption and emission features obtained from the solution and film samples were similar, which suggests that the dendritic nature was preserved in the solid state. Thus, the electronic transitions of the siloles were primarily determined by their molecular structures, which were insensitive to their aggregation state. Further research on silole-incorporated dendrimers, including their application in electroluminescence devices, is now in progress.

Experimental Section

General Procedures. All reactions were carried out under a dry N₂ atmosphere. Tetrahydrofuran (THF) and toluene were dried from sodium benzophenone ketyl. Diphenylacetylene and lithium were purchased from Aldrich Chemicals and used without purification. 2,4,6,8-Tetramethyl-2,4,6,8-tetravinyl-2,4,6,8-tetrasilane-1,3,5,7-tetraoxacyclooctane was purchased from Aldrich Chemicals and dried over molecular sieves (4 Å). Dichloromethylsilane was purchased from Gelest and used after vacuum distillation. A platinum catalyst (Pt on activated carbon, 10% Pt content) was purchased from Strem Chemicals and used after being vacuum-dried at room temperature. The NMR spectra were recorded on a Bruker AC-200 spectrometer. Elemental analysis and MALDI mass spectroscopy (ABI Voyager STR) were performed by the Pusan and Daejeon Branches of the Korean Basic Science Institute. The absorption and photoluminescence spectra were recorded on a Perkin-Elmer Lambda 2S UV–visible spectrophotometer and a Perkin-Elmer LS fluorescence spectrometer, respectively. Molecular weight distributions (*M_w/M_n*) were determined by gel permeation chromatography (GPC) with a Waters instrument equipped with Stragel HR 3, 4, and 5 columns. Cyclic voltammetric experiments were performed using a BAS 100 electrochemical analyzer. A three-electrode cell system was used containing a glassy carbon, a platinum wire, and Ag/AgNO₃ as the working, counter, and reference electrode. Freshly distilled, de-

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gassed CH_2Cl_2 was used as the solvent, with 0.1 M tetrabutylammonium perchlorate as the supporting electrolyte. Potential values were calibrated with respect to Fc^+/Fc (Fc = ferrocene) redox couple. Molecular models were constructed using a Cerius computer modeling program with a 2.21 force field library on a SGI workstation and Materials Studio 3.0 software using the PCFF force field for energy minimization and molecular dynamics.

General Procedure for G1-8Cl. A mixture of 5.2 g (14.94 mmol) of 2,4,6,8-tetramethyl-2,4,6,8-tetravinylcyclotetrasiloxane, 13.80 g (120 mmol) of dichloromethylsilane, and 0.1 g of Pt/C (10% Pt content) in 50 mL of toluene was stirred for 3 h at 50 °C. When the reaction was complete by ^1H NMR, the catalyst was filtered off and washed with pentane under N_2 . The volatile components were removed under reduced pressure, leaving a colorless oil. **G1-8Cl** was obtained as a clear and colorless oil. Yield: 97% (11.66 g, 14.5 mmol).

General Procedure for G1-8Allyl. Allyl alcohol (10.80 g, 186 mmol) in 50 mL of toluene was slowly added to a mixture of 11.6 mmol (9.34 g) of **G1-8Cl** and 186 mmol (21.61 g) of TMEDA in 150 mL of toluene for about 2 h. After the addition was finished, the reaction mixture was heated to 50 °C for 30 min. When the reaction was complete by ^1H NMR, the salt was filtered off and washed with pentane. The volatile components were removed under reduced pressure, leaving a colorless liquid. Products were chromatographed on silica gel with toluene as an eluent. **G1-8Allyl** was obtained as a clear and colorless oil. Yield: 74% (8.39 g, 8.58 mmol).

G2-16Cl. A procedure analogous to the preparation of **G1-8Cl** was used, but starting from 8.6 mmol (8.40 g) of **G1-8Allyl**, 137 mmol (15.76 g) of dichloromethylsilane, and 0.15 g of Pt/C (10% Pt content) in 50 mL of toluene. **G2-16Cl** was obtained as a clear and colorless oil. Yield: 91% (14.84 g, 7.82 mmol).

G2-16Allyl. A procedure analogous to the preparation of **G1-8Allyl** was used, but starting from 7.8 mmol (17.50 g) of **G2-16Cl**, 249 mmol (14.50 g) of allyl alcohol, and 249 mmol (28.93 g) of TMEDA in 150 mL of toluene. **G2-16Allyl** was obtained as a colorless oil. Yield: 76% (13.28 g, 5.92 mmol).

G3-32Cl. A procedure analogous to the preparation of **G1-8Cl** was used, but starting from 3.2 mmol (7.18 g) of **G2-16Allyl**, 102 mmol (11.73 g) of dichloromethylsilane, and 0.1 g of Pt/C (10% Pt content) in 50 mL of toluene. **G3-32Cl** was obtained as a viscous oil. Yield: 90% (11.76 g, 2.88 mmol).

G3-32Allyl. A procedure analogous to the preparation of **G1-8Allyl** was used, but starting from 0.86 mmol (3.51 g) of **G3-32Cl**, 55.04 mmol (3.03 g) of allyl alcohol, and 55.04 mmol (6.40 g) of TMEDA in 150 mL of toluene. **G3-32Allyl** was obtained as a viscous oil. Yield: 60% (2.48 g, 0.52 mmol).

G4-64Cl. A procedure analogous to the preparation of **G1-8Cl** was used, but starting from 0.25 mmol (1.19 g) of **G3-32Allyl**, 16 mmol (1.84 g) of dichloromethylsilane, and 0.1 g of Pt/C (10% Pt content) in 50 mL of toluene. **G4-64Cl** was obtained as a viscous oil. Yield: 88% (1.86 g, 0.22 mmol).

General Procedure for GB0-2Ethylyl. A 160 mmol sample of lithium phenylacetylide (1 M solution in THF) was added dropwisely to dimethyldichlorosilane (8.58 g, 66.48 mmol) in 50 mL of THF. After having been refluxed for 2 h, the solvent was removed under reduced pressure. The salt was precipitated in pentane and filtered off. Products were chromatographed on silica gel with hexane. **GB0-2Ethylyl** was obtained as a white, crystalline solid. Yield: 90% (7.72 g, 59.83 mmol).

General Procedure for GB1-4Cl. A mixture of 18.66 mmol (4.86 g) of **GB0-2Ethylyl**, 74.64 mmol (8.58 g) of dichloromethylsilane, and 0.08 g of Pt/C (10% Pt content) in 25 mL of toluene was refluxed for 6 h. When the reaction was complete by ^1H NMR, the catalyst was filtered off and washed with pentane under N_2 . The volatile components were removed under reduced pressure,

leaving a colorless oil. **GB1-4Cl** was obtained as a colorless oil. Yield: 97% (8.88 g, 18.10 mmol).

GB1-4Ethylyl. A procedure analogous to the preparation of **GB0-2Ethylyl** was used, but starting from 9 mmol (4.41 g) of **GB1-4Cl** and 45 mmol (1 M solution in THF) of lithium phenylacetylide in 50 mL of THF. Products were chromatographed on silica gel with toluene/hexane (1:5). **GB1-4Ethylyl** was obtained as a white, crystalline solid. Yield: 89% (6.03 g, 8.01 mmol).

GB2-8Cl. A procedure analogous to the preparation of **GB1-4Cl** was used, but starting from 4 mmol (3.01 g) of **GB1-4Ethylyl**, 32 mmol (3.68 g) of dichloromethylsilane, and 0.08 g of Pt/C (10% Pt content) in 25 mL of toluene. **GB2-8Cl** was obtained as a slightly yellow gel. Yield: 97% (4.70 g, 3.88 mmol).

GB2-8Ethylyl. A procedure analogous to the preparation of **GB0-2Ethylyl** was used, but starting from 2 mmol (2.43 g) of **GB2-8Cl** and 20 mmol (1 M solution in THF) of lithium phenylacetylide in 50 mL of THF. Products were chromatographed on silica gel with toluene/hexane (1:3). **GB2-8Ethylyl** was obtained as a hard, yellow gel. Yield: 89% (1.78 mmol, 3.09 g).

GB3-16Cl. A procedure analogous to the preparation of **GB1-4Cl** was used, but starting from 1 mmol (1.74 g) of **GB2-8Ethylyl**, 16 mmol (1.84 g) of dichloromethylsilane, and 0.08 g of Pt/C (10% Pt content) in 25 mL of toluene. **GB3-16Cl** was obtained as a yellow gel. Yield: 92% (2.45 g, 0.92 mmol).

General Procedure for G1-4Silole. To a solution of diphenylacetylene (2.25 g, 12.5 mmol) in dry THF (10 mL) were added clean lithium shavings (173 mg, 25 mmol). The reaction mixture was stirred at room temperature for 2 h under a dry argon atmosphere. The mixture was then diluted with 120 mL of THF, followed by the addition of **G1-8Cl** (1.13 g, 1.40 mmol) at 0 °C. After stirring for 12 h at room temperature, the reaction mixture was filtered and the filtrate was washed with water. The organic layer was extracted with CH_2Cl_2 and dried over magnesium sulfate. The solvent was removed and the residue was purified using flash chromatography over silica gel using benzene/hexane (1:1) as eluent. Recrystallization from CH_2Cl_2 /hexane produced a greenish-yellow powder in a 60% yield (1.64 g, 0.84 mmol) based on silane. ^1H NMR (CDCl_3): δ -0.14 (s, 12H, SiCH_3 , G0), 0.39 (s, 12H, SiCH_3 , G1), 0.83–0.88 (m, 16H, CH_2 , G0), 6.74–7.05 (m, 80H, *Ph*, silole). ^{13}C NMR (CDCl_3): δ -5.76 (SiCH_3 , G0), -1.43 (SiCH_3 , G1), 4.59, 8.62 (CH_2 , G0), 125.48, 126.12, 127.37, 127.94, 128.34, 128.74, 130.00, 138.74, 140.03, 154.60 (*Ph*, silole). GPC: PDI (M_w/M_n) 1.004 (1999/1990), t_R 18.32 min. Anal. Calcd for $\text{C}_{128}\text{H}_{120}\text{O}_4\text{Si}_8$: C, 78.96; H, 6.21. Found: C, 78.86; H, 6.12. MS (MALDI): m/z 1946.212 [M] $^+$, 1969.246 [$\text{M} + \text{Na}$] $^+$.

G2-8Silole. A procedure analogous to the preparation of **G1-4Silole** was used, but starting from **G2-16Cl** (1.33 g, 0.70 mmol). The product was isolated by silica gel column chromatography using benzene/hexane (1:1) as an eluent. **G2-8Silole** was obtained as a yellow gel. Yield: 50% (1.46 g, 0.35 mmol) based on silane. ^1H NMR (CDCl_3): δ -0.053 (m, 24H, SiCH_3 , G0-G1), 0.43 (s, 24H, SiCH_3 , G2), 0.81–1.03, 1.42–1.63 (m, 48H, CH_2 , G0-G1), 3.38–3.61 (m, 16H, OCH_2 , G1), 6.70–7.18 (m, 160H, *Ph*, silole). ^{13}C NMR (CDCl_3): δ -5.77 (SiCH_3 , G1), -5.47 (SiCH_3 , G2), -1.46 (SiCH_3 , G0), 4.83, 8.72 (CH_2 , G0), 9.09, 26.54 (CH_2 , G1), 64.77 (OCH_2 , G1), 125.51, 126.16, 127.35, 127.93, 128.32, 128.75, 129.97, 138.69, 139.88, 140.77, 154.79 (*Ph*, silole). GPC: PDI (M_w/M_n): 1.006 (2609/2592); t_R 17.11 min. Anal. Calcd for $\text{C}_{272}\text{H}_{272}\text{O}_{12}\text{Si}_{16}$: C, 78.11; H, 6.55. Found: C, 77.92; H, 6.14.

G3-16Silole. A procedure analogous to the preparation of **G1-4Silole** was used, but starting from **G3-32Cl** (1.22 g, 0.30 mmol). The product was isolated by silica gel column chromatography using ethyl acetate/hexane as an eluent. **G3-16Silole** was obtained as a yellow gel. Yield: 54% (1.40 g, 0.162 mmol) based on silane. ^1H NMR (CDCl_3): δ 0.04 (m, 48H, SiCH_3 , G0-G2), 0.44 (s, 48H, SiCH_3 , G3), 0.88–0.99, 1.40–1.71 (m, 112H, CH_2 , G0-G2), 3.39–3.63 (m, 48H, OCH_2 , G1-G2), 6.64–7.12 (m, 320H, *Ph*, silole).

^{13}C NMR (CDCl_3): δ -5.62 (SiCH_3 , G1), -5.44 (SiCH_3 , G3), -4.87 (SiCH_3 , G2), -1.82 (SiCH_3 , G0), 4.98, 8.72 (CH_2 , G0), 9.59, 26.02 (CH_2 , G1), 9.11, 26.56 (CH_2 , G2), 64.76 (OCH_2 , G1-G2), 125.59, 125.74, 125.92, 126.19, 126.56, 126.92, 127.05, 127.38, 127.95, 128.17, 128.34, 128.47, 128.77, 129.98, 130.38, 130.92, 131.41, 134.33, 138.70, 139.88, 140.76, 141.67, 142.42, 154.76 (*Ph*, silole). PDI (M_w/M_n): 1.016 (3062/3011); t_R 16.65 min. Anal. Calcd for $\text{C}_{560}\text{H}_{576}\text{O}_{28}\text{Si}_{32}$: C, 77.73; H, 6.71. Found: C, 77.41; H, 6.30.

G4-32Silole. A procedure analogous to the preparation of **G1-4Silole** was used, but starting from **G4-64Cl** (1.15 g, 0.136 mmol). The product was isolated by silica gel column chromatography using ethyl acetate/hexane as an eluent. **G4-32Silole** was obtained as a yellow gel. Yield: 30% (0.72 g, 0.04 mmol) based on silane. ^1H NMR (CDCl_3): δ 0.01 (m, 96H, SiCH_3 , G0-G3), 0.43 (s, 96H, SiCH_3 , G4), 0.79-1.03, 1.39-1.70 (m, 240H, CH_2 , G0-G3), 3.51 (m, 112H, OCH_2 , G1-G3), 6.63-7.13 (m, 640H, *Ph*, silole). ^{13}C NMR (CDCl_3): δ -5.54 (SiCH_3 , G2), -5.44 (SiCH_3 , G4), -4.87 (SiCH_3 , G3), -1.82 (SiCH_3 , G0), -1.79 (SiCH_3 , G1), 4.98, 8.60 (CH_2 , G0), 10.89, 22.45 (CH_2 , G1), 9.25, 26.03 (CH_2 , G2), 9.12, 26.56 (CH_2 , G3), 64.75 (OCH_2 , G1-G3), 125.53, 126.19, 127.37, 127.96, 128.77, 129.97, 138.69, 139.87, 154.76 (*Ph*, silole). PDI (M_w/M_n): 1.011 (3240/3204), t_R 16.43 min. Anal. Calcd for $\text{C}_{1136}\text{H}_{1184}\text{O}_{60}\text{Si}_{64}$: C, 77.55; H, 6.78. Found: C, 77.15; H, 6.45.

Preparation of GB1-2Silole. To a solution of diphenylacetylene (2.25 g, 12.5 mmol) in dry THF (10 mL) were added clean lithium shavings (173 mg, 25 mmol). The reaction mixture was stirred at room temperature for 2 h in a dry argon atmosphere. The mixture was then diluted with 120 mL of THF, followed by the addition of **GB1-4Cl** (1.471 g, 3.0 mmol) at 0 °C. After stirring for 2 h at room temperature, the mixture was refluxed for 6 h. The reaction mixture was filtered, then the filtrate was washed with water. The organic layer was extracted with CH_2Cl_2 and dried over magnesium sulfate. The solvent was removed and the residue was purified by flash chromatography on silica gel using benzene/hexane (1:1) as an eluent. **GB1-2Silole** was obtained as a green powder. Suitable crystals for X-ray structure were obtained from slow evaporation of a CH_2Cl_2 /hexane mixture. Yield: 68% (2.16 g, 2.04 mmol) based on silane. ^1H NMR (CDCl_3): δ -0.45 (s, 6H, SiCH_3 , G0), 0.59 (s, 6H, SiCH_3 , G1), 6.50 (s, 2H, $\text{CH}=\text{C}$, G0), 6.56-6.60 (m, 10H, *Ph*, G0), 6.84-7.10 (m, 40H, *Ph*, silole). ^{13}C NMR (CDCl_3): δ -6.94 (SiCH_3 , G1), -0.46 (SiCH_3 , G0), 125.57, 126.08, 126.17, 127.15, 127.24, 127.38, 127.72, 129.11, 129.52, 138.91, 139.02, 139.24, 139.24, 144.54, 155.70 (*Ph*, *Ph*/silole), 148.64, 155.78 ($\text{CH}=\text{C}$, G0). GPC: PDI (M_w/M_n) 1.013 (1085/1070); t_R 19.45 min. Anal. Calcd for $\text{C}_{76}\text{H}_{64}\text{Si}_3$: C, 85.99; H, 6.08. Found: C, 85.88; H, 5.75. MS (MALDI): m/z 1061.186 [M] $^+$, 1084.237 [$\text{M} + \text{Na}$] $^+$.

GB2-4Silole. A procedure analogous to the preparation of **GB1-2Silole** was used, but starting from **GB2-8Cl** (1.69 g, 1.40 mmol). The product was isolated by silica gel column chromatography using benzene/hexane (2:1) as an eluent. **GB2-4Silole** was obtained as a yellow, sticky powder. Yield: 59% (1.95 g, 0.826 mmol) based on silane. ^1H NMR (CDCl_3): δ -0.77 (s, 6H, SiCH_3 , G0), -0.59 (s, 6H, SiCH_3 , G1), 0.51 (s, 12H, SiCH_3 , G2), 5.65 (s, 2H, $\text{CH}=\text{C}$, G0), 6.40 (s, 4H, $\text{CH}=\text{C}$, G1), 6.45-6.62 (m, 30H, *Ph*, G0-G1), 6.68-7.12 (m, 80H, *Ph*, silole). ^{13}C NMR (CDCl_3): δ -6.96 (SiCH_3 , G2), -3.01 (SiCH_3 , G1), -0.30 (SiCH_3 , G0), 125.65, 126.09, 126.24, 127.06, 127.31, 127.40, 127.77, 127.83, 129.12,

129.14, 129.51, 138.74, 139.04, 139.16, 143.18, 144.99, 155.90 (*Ph*, *Ph*/silole), 145.36, 163.18 ($\text{CH}=\text{C}$, G0), 146.00, 160.89 ($\text{CH}=\text{C}$, G1). GPC: PDI (M_w/M_n) 1.005 (2163/2151); t_R 17.99 min. Anal. Calcd for $\text{C}_{168}\text{H}_{140}\text{Si}_7$: C, 85.66; H, 5.99. Found: C, 85.48; H, 5.57. MS (MALDI): m/z 2377.026 [$\text{M} + \text{Na}$] $^+$.

GB3-8Silole. A procedure analogous to the preparation of **GB1-2Silole** was used, but starting from **GB3-16Cl** (1.861 g, 0.70 mmol). The product was isolated by silica gel column chromatography using benzene/hexane (3:1) as an eluent. **GB3-8Silole** was obtained as a hard, yellow gel. Yield: 50% (1.73 g, 0.35 mmol) based on silane. ^1H NMR (CDCl_3): δ -0.89 (s, 12H, SiCH_3 , G2), -0.76 (s, 6H, SiCH_3 , G0), -0.48 (s, 6H, SiCH_3 , G1), 0.50 (s, 24H, SiCH_3 , G3), 5.98 (s, 2H, $\text{CH}=\text{C}$, G0), 6.37 (s, 4H, $\text{CH}=\text{C}$, G1), 6.40 (s, 8H, $\text{CH}=\text{C}$, G2), 6.53-7.13 (m, 230H, *Ph*, *Ph*/silole). ^{13}C NMR (CDCl_3): δ -6.91 (SiCH_3 , G3), -3.19 (SiCH_3 , G2), -2.97 (SiCH_3 , G1), 0.23 (SiCH_3 , G0), 125.27, 125.65, 126.07, 127.04, 127.38, 127.76, 127.85, 128.21, 128.32, 129.09, 129.48, 138.62, 139.05, 139.12, 143.05, 144.57, 155.84 (*Ph*, *Ph*/silole), 146.23, 163.45 ($\text{CH}=\text{C}$, G0), 146.10, 163.24 ($\text{CH}=\text{C}$, G1), 145.42, 162.45 ($\text{CH}=\text{C}$, G2). GPC: PDI (M_w/M_n) 1.007 (2680/2662); t_R 17.04 min. Anal. Calcd for $\text{C}_{352}\text{H}_{292}\text{Si}_{15}$: C, 85.52; H, 5.95. Found: C, 84.92; H, 5.59. MS (MALDI): m/z 4981.72 [$\text{M} + \text{K}$] $^+$.

Crystal Structure Determination and Computational Details. Crystals of **GB1-4Ethyne** and **GB1-2Silole** were obtained from CH_2Cl_2 /hexane, sealed in glass capillaries under argon, and mounted on the diffractometer. Preliminary examination and data collection were performed using a Bruker SMART CCD detector system single-crystal X-ray diffractometer equipped with a sealed-tube X-ray source (40 kV \times 50 mA) using graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). Preliminary unit cell constants were determined with a set of 45 narrow-frame (0.3° in ω) scans. The double-pass method of scanning was used to exclude any noise. The collected frames were integrated using an orientation matrix determined from the narrow-frame scans. The SMART software package was used for data collection, and SAINT was used for frame integration.^{21a} Final cell constants were determined by a global refinement of xyz centroids of reflections harvested from the entire data set. Structure solution and refinement were carried out using the SHELXTL-PLUS software package.^{21b} Molecular models for **G4-32Silole** are created using Cerius software.²²

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Note Added after ASAP Publication. In the version of this paper published on the Web December 15, 2005, Scheme 3 was incorrect. The version that now appears in this paper is correct.

Supporting Information Available: This material is available free of charge via the Internet at <http://pubs.acs.org>.

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