

# Synthesis of Water-Soluble Carbosilane Dendrimers

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**Abstract:** Nucleophilic reactions between mercapto-substituted amphiphiles and carbosilane dendrimers bearing (chloromethyl)silyl groups on their terminal branches gave, in high yields, amphiphilic dendrimers with hydrophobic carbosilane cores and alcohol, dimethylamino, or sodium sulfonate amphiphilic groups at the periphery. The negatively charged, sulfonate-terminated dendrimers were soluble in water, as were positively charged poly(ammonium) salts prepared from the dimethylamino-terminated derivatives. These new amphiphilic dendrimers were characterized by spectroscopic and mass spectrometric techniques. Preliminary studies of the aqueous solution behavior of the second generation, sulfonate-terminated dendrimer demonstrated its ability to enhance the solubility of lipophilic alkyl-substituted benzene derivatives, a characteristic property of micelles.

## Introduction

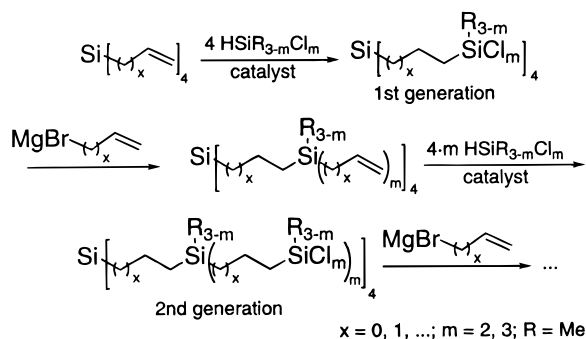
As the science of dendrimer synthesis continues to mature, there is an increasing focus on developing applications for dendrimers that exploit their unique topology.<sup>1–5</sup> One such application employs dendrimers bearing amphiphilic groups on their terminal branches as model systems to mimic both the structure and the physical properties of micelles. Like micelles, these amphiphilic dendrimers possess a globular structure, with a relatively nonpolar core and a hydrophilic outer surface. Numerous examples of amphiphilic dendrimers have been reported, based on a variety of different dendrimer backbone constructions: poly(ethers),<sup>6–8</sup> poly(amides),<sup>9–13</sup> poly(amidoamines),<sup>14–17</sup> poly(esters),<sup>18</sup> and others.<sup>19–23</sup> Many of these have exhibited solution properties typically associated with micelles,

e.g., the solubilization of host molecules into water<sup>6,19,21</sup> or other solvents,<sup>24,25</sup> interactions with spectroscopic probe molecules,<sup>14,15,17,21,26–29</sup> partitioning of solutes in micellar electrokinetic capillary chromatography,<sup>30,31</sup> and catalysis.<sup>7,32–36</sup>

Nearly all amphiphilic dendrimers synthesized to date have contained polar groups (e.g., amines, ethers, esters, and amides) in their backbones, despite the fact that those with completely hydrophobic backbones would be expected to more closely

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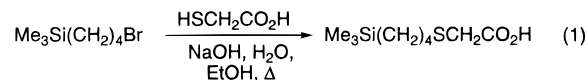
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**Scheme 1.** Divergent Synthesis of Carbosilane Dendrimers

mimic the hydrophobic environment found in the interior of micelles.<sup>37</sup> Although Newkome and co-workers have reported the successful production of water-soluble dendrimers with completely hydrophobic hydrocarbon backbones, their procedures involved multistep syntheses, with low overall yields.<sup>20–22</sup> Recently, several groups, including our own, have reported high-yield, divergent syntheses of completely hydrophobic carbosilane dendrimers starting from readily available materials: by using repeating sequences of alternating hydrosilylations with substituted chlorosilanes and alkenylations with Grignard reagents, several generations of either chlorosilyl- or alkenylsilyl-terminated dendrimers with varying alkenyl chain lengths have been synthesized (Scheme 1).<sup>38–41</sup> Various groups have employed these dendrimers as frameworks upon which to attach other functional groups.<sup>42–54</sup> However, so far there have been no reported attempts to fit these dendrimers with terminal amphiphilic groups, although two groups have reported the synthesis of hydroxyl-terminated carbosilane dendrimers.<sup>23,55</sup>

To synthesize stable amphiphilic carbosilane dendrimers, a method was sought by which amphiphilic moieties could be attached to the carbosilane framework through moisture-stable

linkages. Since most silicon-heteroatom (e.g., Si–N, Si–OR, Si–S) bonds are moisture sensitive,<sup>32,56</sup> simple nucleophilic reactions with chlorosilyl-terminated dendrimers would not be suitable. In 1953, Perklev reported the functionalization of a (bromoalkyl)silane with a mercapto-substituted carboxylic acid (eq 1).<sup>57</sup> Since the amphiphilic group in this example was



attached to the organosilicon moiety by a moisture-stable C–S bond, this methodology seemed promising for the production of amphiphilic carbosilane dendrimers. In this report, we describe the high-yield synthesis of amphiphilic carbosilane dendrimers through the reaction of (chloromethyl)silyl-terminated carbosilane dendrimers with several mercapto-substituted amphiphilic compounds. The (chloromethyl)silyl-substituted carbosilane dendrimers were obtained by hydrosilylation of previously reported<sup>40</sup> vinylsilane-terminated dendrimers with (chloromethyl)dimethylsilane.

## Results and Discussion

**Preparation of (Chloromethyl)silyl-Terminated Dendrimers.** Vinylsilane-terminated dendrimers were synthesized according to the method of Zhou and Roovers, using tetraalkenylsilane as the initiator core, methylchlorosilane in the hydrosilylation step, and vinylmagnesium bromide in the alkenylation step (Scheme 1;  $m = 2, x = 0, R = \text{Me}$ ).<sup>40</sup> Zeroth, first, and second generation, (chloromethyl)silyl-terminated dendrimers **OG-4CH<sub>2</sub>Cl**, **1G-8CH<sub>2</sub>Cl**, and **2G-16CH<sub>2</sub>Cl** were obtained, respectively, from the platinum-catalyzed hydrosilylation of tetraalkenylsilane and the first and second generation, vinyl-terminated dendrimers **1G-8Vi** and **2G-16Vi** with excess HSiMe<sub>2</sub>CH<sub>2</sub>Cl (Scheme 2). This hydrosilylation reaction was found to be effervescent and strongly exothermic, necessitating the slow addition of HSiMe<sub>2</sub>CH<sub>2</sub>Cl to the reaction mixture in order to avoid explosions. In all cases the terminal vinyl groups reacted completely with HSiMe<sub>2</sub>CH<sub>2</sub>Cl to give dendrimers with monodisperse GPC traces and no residual vinyl resonances in their <sup>1</sup>H NMR spectra. The zeroth and first generation dendrimers were crystalline solids, but the second generation was an oil.

The hydrosilylation of a vinylsilane, R<sub>3</sub>SiCH=CH<sub>2</sub>, with HSiMe<sub>2</sub>CH<sub>2</sub>Cl may form two regioisomers, the α-addition product, R<sub>3</sub>SiCH(CH<sub>3</sub>)SiMe<sub>2</sub>CH<sub>2</sub>Cl, and the β-addition product, R<sub>3</sub>SiCH<sub>2</sub>CH<sub>2</sub>SiMe<sub>2</sub>CH<sub>2</sub>Cl. The presence of a mixture of such isomers in a dendrimer does not alter its molecular weight or its number of branches, and should not result in dramatic changes to its overall shape.

In the hydrosilylation of vinyl-terminated dendrimers with HSiMe<sub>2</sub>CH<sub>2</sub>Cl, both α- and β-addition isomers were formed. The β-addition product predominated, but α-addition isomers were detected in the <sup>1</sup>H NMR spectra of the crude product mixtures (in amounts of 4–9%) by the observation of a characteristic doublet ( $J = 8 \text{ Hz}$ ) at 1.0 ppm.<sup>58</sup> Dendrimers containing unwanted α-addition isomers in the terminal branches could be removed from crude product mixtures of **OG-4CH<sub>2</sub>Cl** and **1G-8CH<sub>2</sub>Cl** by recrystallization, giving spectroscopically pure products in 67% and 52% yield, respectively. Since the second generation dendrimer **2G-16CH<sub>2</sub>Cl** was not crystalline,

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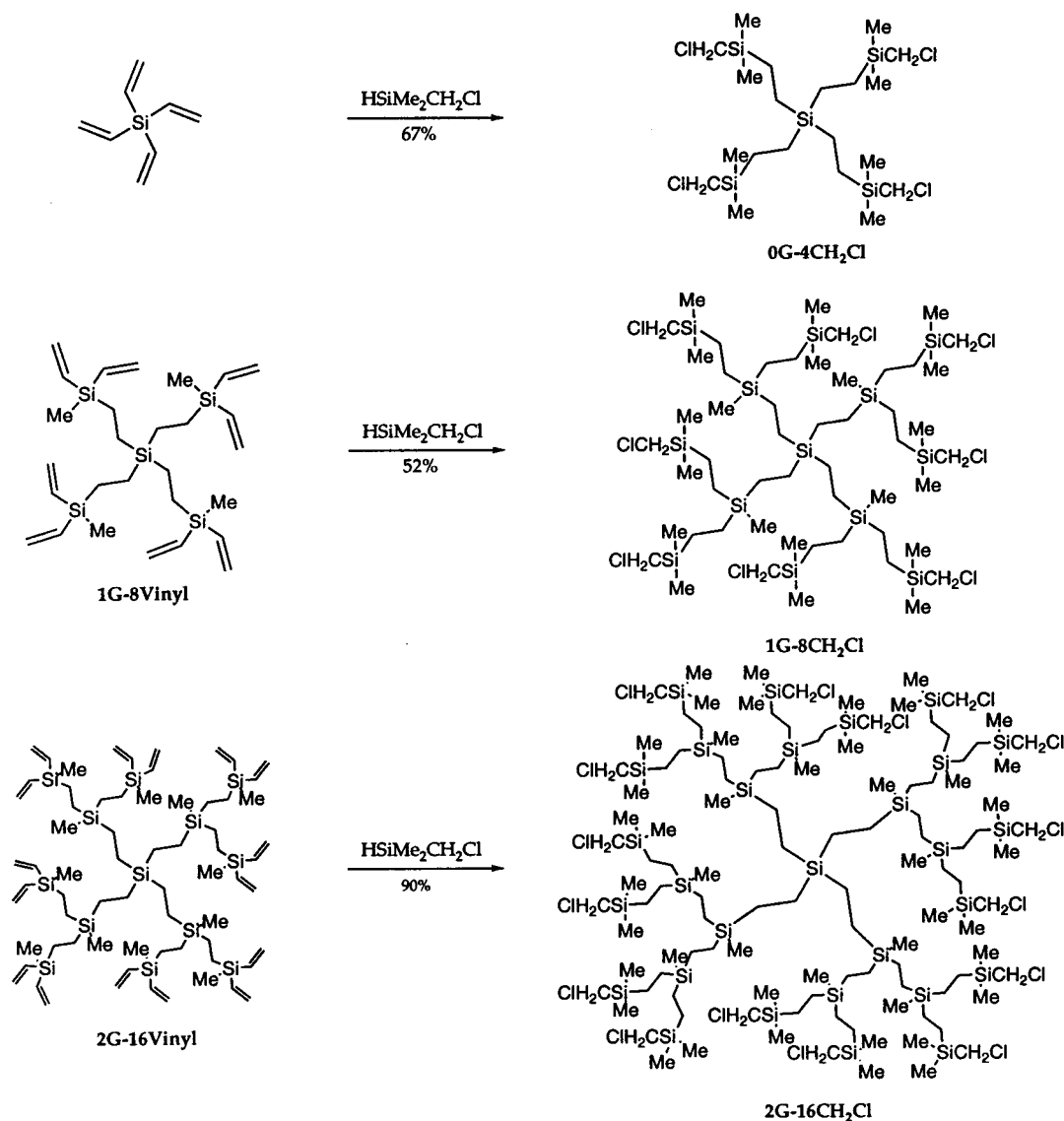
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**Scheme 2.** Synthesis of (Chloromethyl)silyl-Terminated Dendrimers

there was no way to remove the 9%  $\alpha$ -addition products present in its terminal branches. The  $\alpha$ -addition isomers are expected to be randomly distributed among the individual dendrimer molecules, with different molecules bearing differing numbers of  $\alpha$ -addition isomers on their terminal branches. Using a mathematical treatment,<sup>59</sup> one can predict that out of 100 molecules of **2G-16CH<sub>2</sub>Cl**, the number of molecules possessing 0, 1, 2, 3, 4, and 5  $\alpha$ -addition isomers among their 16 terminal branches will be 22, 35, 26, 12, 4 and 1, respectively.

The <sup>1</sup>H, <sup>13</sup>C, and <sup>29</sup>Si NMR spectra of **OG-4CH<sub>2</sub>Cl**, **1G-8CH<sub>2</sub>Cl**, and **2G-16CH<sub>2</sub>Cl** displayed sharp, well-resolved resonances for all nuclei except the innermost methylene groups of the second generation dendrimer, whose <sup>1</sup>H and <sup>13</sup>C NMR signals were somewhat broadened.

**Attachment of Amphiphilic Groups.** As illustrated in Scheme 3, amphiphilic groups were attached to the terminal branches of carborane dendrimers via thioether linkages. The

(58) The syntheses of **1G-8Vi** and **2G-16Vi** also produced approximately 10%  $\alpha$ -addition isomers in each hydrosilylation step. Upon further hydrosilylation with HSiMe<sub>2</sub>CH<sub>2</sub>Cl, these isomers became spectroscopically undetectable. The  $\alpha$ -addition isomers referred to in the text are those produced during the hydrosilylation with HSiMe<sub>2</sub>CH<sub>2</sub>Cl. Approaches for removing unwanted  $\alpha$ -addition isomers from **1G-Vi** and **2G-16Vi** are the subject of a forthcoming publication: Krska, S. W.; Seyferth, D. Manuscript in preparation.

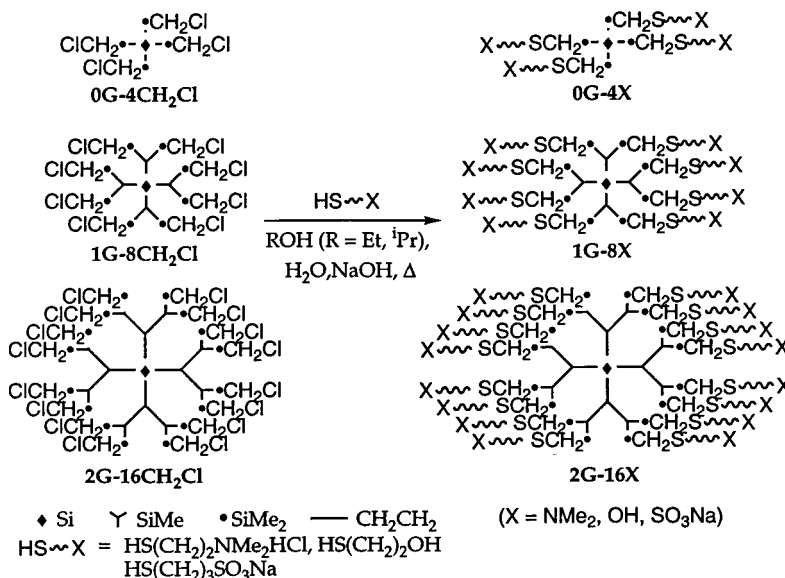
syntheses involved deprotonating amphiphile-substituted mercaptans with NaOH and reacting the resulting thiolates with chloromethyl-terminated dendrimers **OG-4CH<sub>2</sub>Cl**, **1G-8CH<sub>2</sub>Cl**, and **2G-16CH<sub>2</sub>Cl** in alcohol/water solvent mixtures (ethanol was used for **OG-4CH<sub>2</sub>Cl**, and 2-propanol for **1G-8CH<sub>2</sub>Cl** and **2G-16CH<sub>2</sub>Cl**). Reaction mixtures were initially biphasic, but clarified over time with heating; extra water or alcohol was added as needed to assist in the dissolution of all reagents. In most cases, quantitative substitution of all chloromethyl groups occurred within several hours. In those cases where some chloromethyl groups remained unreacted at the termination of the reaction, complete substitution was effected by reapplication

(59) Given a dendrimer with  $P$  identical reactive endgroups which undergo a chemical transformation to  $n$  different types of groups  $a_1, a_2, \dots, a_n$  present in the final product mixture in the proportions  $q_1, q_2, \dots, q_n$ , the composition of individual dendrimer molecules in the product mixture may be expressed as  $a_1^{k_1}a_2^{k_2}\dots$ , where  $k_1, k_2, \dots, k_n$  are the numbers of endgroups in the product dendrimer bearing the groups  $a_1, a_2, \dots, a_n$ , and  $k_1 + k_2 + \dots + k_n = P$ . The mole fraction  $X_{a_1^{k_1}a_2^{k_2}\dots}$  of dendrimers with composition  $a_1^{k_1}a_2^{k_2}\dots$  is given by:

$$X_{a_1^{k_1}a_2^{k_2}\dots} = \left( \frac{P!}{k_1!k_2!\dots} \right) q_1^{k_1}q_2^{k_2}\dots$$

A special case of this formula, applicable to PAMAM dendrimers, may be found in ref 1.

## Scheme 3. Synthesis of Amphiphile-Terminated Dendrimers



**Table 1.** Attachment of Amphiphilic Groups to Chloromethyl-Terminated Dendrimers

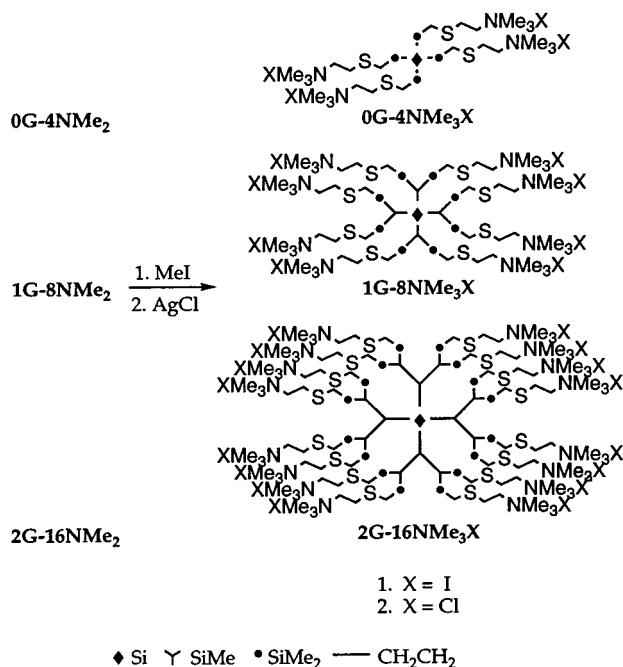
chloromethyl-terminated dendrimer	mercapto-substituted amphiphile	product	yield, %
OG-4CH <sub>2</sub> Cl	HSCH <sub>2</sub> CH <sub>2</sub> OH	OG-4OH	98
1G-8CH <sub>2</sub> Cl	HSCH <sub>2</sub> CH <sub>2</sub> OH	1G-8OH	99
OG-4CH <sub>2</sub> Cl	HSCH <sub>2</sub> CH <sub>2</sub> NMe <sub>2</sub> HCl	OG-4NMe <sub>2</sub>	100
1G-8CH <sub>2</sub> Cl	HSCH <sub>2</sub> CH <sub>2</sub> NMe <sub>2</sub> HCl	1G-8NMe <sub>2</sub>	92
2G-16CH <sub>2</sub> Cl	HSCH <sub>2</sub> CH <sub>2</sub> NMe <sub>2</sub> HCl	2G-16NMe <sub>2</sub>	92
OG-4CH <sub>2</sub> Cl	HSCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> SO <sub>3</sub> Na	OG-4SO <sub>3</sub> Na	80
1G-8CH <sub>2</sub> Cl	HSCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> SO <sub>3</sub> Na	1G-8SO <sub>3</sub> Na	66
2G-16CH <sub>2</sub> Cl	HSCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> SO <sub>3</sub> Na	2G-16SO <sub>3</sub> Na	75

of the reaction procedure. Products and yields of these reactions are given in Table 1.

All of the substitutions listed in Table 1 proceeded without any observable side reactions. The alcohol- and dimethylamino-terminated dendrimers were soluble in organic solvents and completely insoluble in water. The zeroth generation, alcohol-terminated dendrimer **OG-4OH** was a crystalline solid. Its first generation analogue **1G-8OH** was a viscous oil, as were the dimethylamino-terminated dendrimers **OG-4NMe<sub>2</sub>**, **1G-8NMe<sub>2</sub>**, and **2G-16NMe<sub>2</sub>**. Dendrimeric products bearing terminal sodium sulfonate groups were obtained as hygroscopic white solids which were completely soluble in water and essentially insoluble in all organic solvents, including alcohols. Removal of the NaCl byproduct and excess NaOH from these dendrimers was accomplished by acidifying aqueous solutions of the crude products to neutral pH and dialyzing in cellulose ester membranes with low molecular weight cutoff values (100–500 daltons). Results of combustion analyses of samples of **OG-4SO<sub>3</sub>Na** and **2G-16SO<sub>3</sub>Na** which had been purified in this manner suggested nearly complete removal of sodium chloride. Results for **1G-8SO<sub>3</sub>Na** purified under similar conditions, however, indicated the presence of 5% (w/w) residual NaCl.

Further reactions involving the dimethylamino-terminated dendrimers **OG-4NMe<sub>2</sub>**, **1G-8NMe<sub>2</sub>**, and **2G-16NMe<sub>2</sub>** converted them into water-soluble derivatives. Protonating their terminal dimethylamino groups with HCl(aq) gave the water-soluble hydrochloride adducts **OG-4NMe<sub>2</sub>HCl**, **1G-8NMe<sub>2</sub>HCl**, and **2G-16NMe<sub>2</sub>HCl**. The zeroth generation hydrochloride adduct was a crystalline solid; higher generations were amorphous solids. Reactions of the dimethylamino-terminated dendrimers with excess MeI<sup>60</sup> provided the quaternary am-

**Scheme 4.** Synthesis of Dendrimers Terminated with Quaternary Ammonium Salts.



monium iodide salts **OG-4NMe<sub>3</sub>I**, **1G-8NMe<sub>3</sub>I**, and **2G-16NMe<sub>3</sub>I** in high yields as analytically pure white powders (Scheme 4). Metathesizing the iodide counterions of these compounds for chloride ions with AgCl<sup>61</sup> greatly enhanced their solubilities in water. The masses of the hygroscopic solids obtained from the metathesis reactions suggested that complete exchange of counterions had occurred; this was corroborated by the results of combustion analyses.

The <sup>1</sup>H, <sup>13</sup>C, and <sup>29</sup>Si NMR spectra of the amphiphilic dendrimers were in most cases consistent with their proposed structures. Line widths for water-soluble derivatives tended to be broader than those of derivatives soluble in organic solvents, presumably a result of dipolar broadening effects arising from

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**Table 2.** Results of MALDI-TOF Mass Spectrometry of Dendrimers

compound	matrix <sup>a</sup> /solvent	molecular ion obsd	calcd mass <sup>b</sup>	measd mass <sup>b</sup>
<b>OG-4CH<sub>2</sub>Cl</b>	CSA, Ag(tfa), ethanol	[M + Ag] <sup>+</sup>	675.04 <sup>c</sup>	674.72 <sup>c</sup>
<b>1G-8CH<sub>2</sub>Cl</b>	CSA, Ag(acac), 2-propanol	[M + Ag] <sup>+</sup>	1499.33 <sup>c</sup>	1499.21 <sup>c</sup>
<b>2G-16CH<sub>2</sub>Cl</b>	CSA, Ag(acac), acetone	[M + Ag] <sup>+</sup>	3161.06	3159.86
<b>OG-4OH</b>	DHB, Na(cit), 2-propanol	[M + Na] <sup>+</sup>	759.27 <sup>c</sup>	759.24 <sup>c</sup>
<b>1G-8OH</b>	DHB, Na(cit), 2-propanol	[M + Na] <sup>+</sup>	1751.71 <sup>c</sup>	1752.06 <sup>c</sup>
<b>OG-4NMe<sub>2</sub></b>	CSA, ethanol	[M + H] <sup>+</sup>	845.48 <sup>c</sup>	845.42 <sup>c</sup>
<b>1G-8NMe<sub>2</sub></b>	CSA, ethanol	[M + H] <sup>+</sup>	1946.10 <sup>c</sup>	1945.68 <sup>c</sup>
<b>2G-16NMe<sub>2</sub></b>	DNB, water	[M + H] <sup>+</sup>	4154.00	4152.28
<b>OG-4SO<sub>3</sub>Na<sup>d</sup></b>	DHB, NH <sub>4</sub> (cit), water	[M - H] <sup>-</sup>	1047.19 <sup>c</sup>	1047.56 <sup>c</sup>
<b>1G-8SO<sub>3</sub>Na<sup>d</sup></b>	DHB, NH <sub>4</sub> (cit), water	[M - H] <sup>-</sup>	2355.31	2354.72
<b>2G-16SO<sub>3</sub>Na<sup>d</sup></b>	DHB, NH <sub>4</sub> (cit), water	[M - H] <sup>-</sup>	4968.25	4967.06
<b>OG-4NMe<sub>3</sub>I</b>	DHB, water	[M + 3 DHB] <sup>-</sup>	1365.27	1365.56
<b>1G-8NMe<sub>3</sub>I</b>	DHB, water	[M + 7 DHB] <sup>-</sup>	3140.27	3142.20
<b>OG-4NMe<sub>3</sub>Cl</b>	DHB, water	[M + 3 DHB] <sup>-</sup>	1365.27	1364.42
<b>1G-8NMe<sub>3</sub>Cl</b>	DHB, water	[M + 7 DHB] <sup>-</sup>	3140.27	3142.20

<sup>a</sup> CSA = 5-chlorosalicylic acid; tfa = trifluoroacetate; acac = acetylacetonate; cit = citrate; DHB = 2,5-dihydroxybenzoic acid. <sup>b</sup> Masses given are weighted isotopic averages, unless otherwise indicated. <sup>c</sup> Monoisotopic mass. <sup>d</sup> Analyzed as the free acid; see ref 71.

the expected decrease in mobility of these predominantly hydrophobic dendrimers in water.<sup>62</sup> The <sup>1</sup>H NMR spectra of the water-soluble dendrimeric ammonium salts unexpectedly exhibited shoulders on the signals associated with the terminal amphiphilic branches; in some cases, shoulders also were observed in the <sup>13</sup>C NMR spectra. Given that these shoulders were not observed in the <sup>1</sup>H or <sup>13</sup>C NMR spectra of the amine-terminated starting materials and that the conversion of terminal amine to quaternary ammonium groups was judged quantitative by elemental analysis and MALDI-TOF mass spectrometry (vide infra), the presence of these extra signals may be most easily explained by the effects of aggregation. Consistent with this explanation, the intensities of shoulders on the NMe and SiCH<sub>2</sub>S resonances in the <sup>1</sup>H NMR spectrum of **OG-4NMe<sub>3</sub>I** varied with the dendrimer's concentration in CD<sub>3</sub>OD.<sup>63</sup>

**MALDI-TOF Mass Spectrometry Measurements.** Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS) has emerged as an invaluable tool for confirming the identities and molecular weight distributions of dendrimers.<sup>23,64–70</sup> So far, there has been only one reported example of the use of MALDI-TOF-MS to characterize carbosilane dendrimers.<sup>23</sup>

A detailed presentation and analysis of the MALDI-TOF mass spectra of the dendrimers synthesized in the present study is being reported separately.<sup>71,72</sup> For purposes of the present discussion, two features of these spectra deserve mention. First of all, the molecular ion peaks, which were observed for all

species except **2G-16NMe<sub>3</sub>X** (X = I, Cl), occurred at *m/z* values which agreed very closely with calculated values (Table 2). For those compounds whose mass spectra could be obtained at isotopic resolution (noted in Table 2), the close correspondence between calculated and experimentally observed isotopic distributions provided further proof of the identities of the compounds in question.

Peaks appearing at *m/z* values lower than that of the molecular ion may arise either from ion fragmentation processes or from lower molecular weight impurities in the dendrimer products. These impurities could originate from incomplete reactions during the dendrimer backbone construction or during the attachment of the amphiphilic groups. To distinguish between fragment ions and impurities, one must rely on the relative intensities of the peaks as well as their masses. Incomplete reactions during the dendrimer synthesis will lead to statistical distributions<sup>59</sup> of lower-molecular-weight compounds whose *m/z* values in the MALDI-TOF mass spectrum should differ from that of the parent ion by multiples of the missing monomer unit.<sup>73</sup>

MALDI-TOF mass spectra of zeroth and first generation dendrimers exhibited few lower mass peaks, and none assignable to dendrimers with missing branches or amphiphilic groups. Only fragment ions were observed,<sup>74</sup> arising primarily from the loss of NaOH for hydroxyl-terminated derivatives and S=CH-(CH<sub>2</sub>)<sub>n</sub>X (n = 1, 2; X = NMe<sub>2</sub>, NMe<sub>3</sub><sup>+</sup>DHB<sup>-</sup>, SO<sub>3</sub>H; DHB<sup>-</sup> = 2,5-dihydroxybenzoate) groups for the other amphiphilic derivatives. Thus, we conclude that these dendrimers do not contain significant amounts of lower molecular weight impurities.

Spectra of second generation dendrimers generally contained more lower mass peaks. The more prominent of these had *m/z* values corresponding to fragment ions (arising from loss of Me<sub>2</sub>-Si=CHCl and CH<sub>3</sub>CH<sub>2</sub>SiMe<sub>2</sub>CH<sub>2</sub>Cl groups for **2G-16CH<sub>2</sub>Cl**, S=CHCH<sub>2</sub>NMe<sub>2</sub> groups for **2G-16NMe<sub>2</sub>**, and S=CH(CH<sub>2</sub>)<sub>2</sub>-SO<sub>3</sub>H groups for **2G-16SO<sub>3</sub>Na**); there were no signals assignable to dendrimers with missing branches or endgroups.<sup>75</sup> However, it was not possible to assign the weaker lower mass peaks in the spectra of **2G-16NMe<sub>2</sub>** and **2G-16SO<sub>3</sub>Na**, and thus the presence of lower molecular weight impurities in these compounds could not be ruled out entirely.<sup>76</sup>

**Solubilization Studies.** Several groups have reported the enhancement of the water solubility of lipophilic compounds

(73) A good example of statistical distributions of lower molecular weight impurities may be found in the MALDI-TOF spectra of ref 23.

(74) Fragment ions have been observed in the MALDI-TOF mass spectra of other dendrimers.<sup>70</sup>

(62) Bovey, F. A. *High-Resolution NMR of Macromolecules*; Academic Press: New York, 1972; p 462.

(63) These shoulders are not believed to be due to  $\alpha$ -addition isomers since they appear prominently in the <sup>1</sup>H NMR spectrum of **OG-4NMe<sub>3</sub>I**, which does not contain  $\alpha$ -addition isomers.

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(72) MALDI-TOF mass spectra for **OG-4OH**, **1G-8OH**, **2G-16CH<sub>2</sub>Cl**, **2G-16NMe<sub>2</sub>**, and **2G-16SO<sub>3</sub>Na** are included in the Supporting Information; for mass spectra of other dendrimers, see ref 71.

in the presence of amphiphilic dendrimers.<sup>6,19,21,77</sup> This type of behavior is one of the signature properties of micelles, and is utilized in a variety of applications ranging from soaps and detergents<sup>78</sup> to micelle-based chromatographic separations.<sup>79</sup> Recently, Hawker et al. reported that poly(aryl ether) dendrimers bearing terminal carboxylate groups were able to significantly enhance the solubility of pyrene and other polycyclic aromatic compounds into water.<sup>6</sup> The extent of solubilization varied linearly with the concentration of dendrimer, which is the same behavior that is observed for surfactant solutions above the CMC.<sup>80</sup> To test whether the dendrimers synthesized in the present study might also exhibit micelle-like solution properties, a preliminary study was undertaken to determine the ability of **2G-16SO<sub>3</sub>Na** to enhance the solubilities of lipophilic compounds in water.

Aqueous solutions of **2G-16SO<sub>3</sub>Na** showed no appreciable solubilization of naphthalene or anthracene (as measured by UV-vis spectroscopy) under conditions similar to those reported in the study discussed above. The extent of solubilization of hydrophobic compounds in micellar solutions typically increases with the inherent aqueous solubility of the organic solubilize.<sup>80</sup> Thus, three compounds—toluene, ethylbenzene, and propylbenzene—with aqueous solubilities ( $5.4 \times 10^{-3}$ ,  $1.65 \times 10^{-3}$ , and  $9.98 \times 10^{-4}$  M, respectively)<sup>81</sup> greater than those of naphthalene ( $2.2 \times 10^{-4}$  M)<sup>82</sup> and anthracene ( $2.2 \times 10^{-7}$  M)<sup>82</sup> were chosen to test the solubilizing ability of **2G-16SO<sub>3</sub>Na**. Since the UV absorbance peaks of these compounds were obscured by dendrimer absorbances, their concentrations in aqueous (D<sub>2</sub>O) solutions of **2G-16SO<sub>3</sub>Na** were measured by comparing the integrated areas of the solubilize peaks to those of the dendrimer (whose concentration was known) in the <sup>1</sup>H NMR spectra. Figure 1 shows the results of these studies for three different concentrations of **2G-16SO<sub>3</sub>Na**. The concentrations of all three organic compounds increased linearly with the concentration of dendrimer, as expected. Extrapolation of these results to zero dendrimer concentration gave values for the inherent solubilities of the three organic compounds C<sub>6</sub>H<sub>5</sub>R in D<sub>2</sub>O ( $3.0 \times 10^{-3}$ ,  $4.7 \times 10^{-4}$ , and  $2.2 \times 10^{-4}$  for R = CH<sub>3</sub>, CH<sub>3</sub>CH<sub>2</sub>, and CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>, respectively) which were in qualitative agreement with the literature values for aqueous solubility.<sup>81</sup> The solubility enhancement corresponded to roughly 2 to 3 alkylbenzene molecules solubilized per dendrimer molecule.<sup>83</sup>

(75) In addition, spectra of the second generation dendrimers each exhibited a sharp, relatively intense peak at approximately one-half the mass of the molecular ion, accompanied by fragment ions of the type discussed in the text. The *m/z* values of these peaks do not correlate with doubly charged ions or with any conceivable fragment ions or lower molecular weight impurities.

(76) Such defects, if present, must be of low abundance, since a second generation dendrimer with as little as 1% missing branches should contain 14% of the dendrimers missing 1 of the 16 branches, giving rise to a prominent peak in the mass spectrum.<sup>59</sup>

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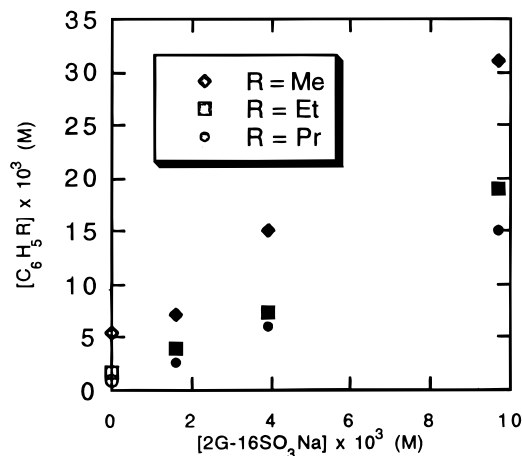
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**Figure 1.** Solubilization of Alkyl-Substituted Benzene Derivatives by **2G-16SO<sub>3</sub>Na**. (Closed symbols represent experimental data; open symbols represent literature solubility values.)

## Experimental Section

**General Comments.** All reactions, unless otherwise noted, were performed under an argon atmosphere with standard Schlenk techniques. Solvents were purified by established procedures. Chlorosilanes were purchased from United Chemical Technologies and distilled from magnesium turnings before use. Tetravinylsilane (95% purity) was purchased from Gelest and used as received. Karstedt catalyst (Pt divinyltetramethyldisiloxane complex)<sup>84–88</sup> solutions were purchased from United Chemical Technologies (2–3 wt % Pt in xylenes) and used as received. 2-Mercaptoethanol, 2-(dimethylamino)ethanethiol hydrochloride and the sodium salt of 3-mercapto-1-propanesulfonic acid were purchased from Aldrich Chemical Co. and used as received. (Chloromethyl)dimethylsilane<sup>89</sup> and the first and second generation, vinyl-terminated dendrimers **1G-8Vi** and **2G-16Vi**<sup>40,58</sup> were synthesized according to literature procedures. Dialyses of sodium sulfonate-terminated dendrimers were carried out in Spectra/Por DispoDialyzer Cellulose Ester membranes with molecular weight cutoff (MWCO) values of 100 and 500 daltons, purchased from Spectrum.

<sup>1</sup>H NMR spectra were obtained at 300 MHz, <sup>13</sup>C NMR spectra were obtained at 75.4 MHz, and <sup>29</sup>Si NMR spectra were obtained at 59.6 MHz. For <sup>29</sup>Si NMR spectra and for <sup>13</sup>C NMR spectra taken in D<sub>2</sub>O, TMS was employed as an external standard. GPC molecular weight determinations were made with a Waters Millipore 150-C ALC/GPC chromatograph equipped with a three-column setup (Waters Ultrastaygel 10<sup>4</sup>, 10<sup>3</sup> Å; Waters μPorasil GPC 60 Å) and toluene as the eluent; molecular weights given are relative to polystyrene standards. MALDI-TOF mass spectrometric measurements were performed by Z. C. Wu and K. Biemann, MIT, and are discussed in detail elsewhere.<sup>71</sup> Elemental analyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark, Galbraith Laboratories, Inc., Knoxville, TN, and E+R Microanalytical Laboratory, Inc., Corona, NY.

**Preparation of OG-4CH<sub>2</sub>Cl.** Tetravinylsilane (4.0 g, 30 mmol) was combined with approximately 2 g of a total of 13.8 g of (chloromethyl)dimethylsilane (127 mmol) and 75 mL of dry THF in a 200 mL three-necked, round-bottomed flask equipped with a reflux condenser, magnetic stir bar, and two rubber septa. Three drops of

(83) The extent of solubilization is similar in magnitude to that observed for the solubilization of polycyclic aromatic compounds by carboxylated poly(benzylaryl ether) dendrimers.<sup>6</sup>

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Karstedt catalyst were added. After approximately 1 min of stirring a strong exotherm was noted. After the solution began to cool, it was immersed in a 40–50 °C oil bath, and the rest of the silane was added over 20 min. After being stirred for 3 h, the reaction mixture was cooled to room temperature, and all volatiles were removed at reduced pressure, leaving a slightly brown, semicrystalline solid. This was recrystallized from hot ethanol, giving **OG-4CH<sub>2</sub>Cl** as colorless needles (12.44 g, 67%): mp 56–57 °C; IR (NaCl disk) 2955 (s), 2903 (s), 2881 (s), 2785 (m), 1395 (s), 1247 (s), 1173 (m), 1129 (s), 1104 (m), 1054 (s), 842 (s); <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 0.085 (s, 24 H, CH<sub>3</sub>), 0.45 (s, br, 16 H, CH<sub>2</sub>CH<sub>2</sub>), 2.78 (s, 8 H, CH<sub>2</sub>Cl); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ -5.11 (CH<sub>3</sub>), 2.31 (SiCH<sub>2</sub>CH<sub>2</sub>SiCH<sub>2</sub>Cl), 5.60 (SiCH<sub>2</sub>CH<sub>2</sub>SiCH<sub>2</sub>Cl), 29.89 (CH<sub>2</sub>Cl); <sup>29</sup>Si NMR (CDCl<sub>3</sub>) δ 5.11 (4 Si, SiCH<sub>2</sub>Cl), 9.82 (1 Si, Si(CH<sub>2</sub>CH<sub>2</sub>)<sub>4</sub>); GPC *M<sub>w</sub>* = 509, *M<sub>n</sub>* = 480 (Calcd *M<sub>n</sub>* = 571), *D* = 1.06. Anal. Calcd for C<sub>20</sub>H<sub>48</sub>Cl<sub>4</sub>Si<sub>5</sub>: C, 42.08; H, 8.48. Found: C, 42.32; H, 8.40.

**Preparation of 1G-8CH<sub>2</sub>Cl.** The above procedure was used in the reaction of 3.37 g of **1G-8Vi** (6.36 mmol) with 7.26 g of (chloromethyl)dimethylsilane (66.8 mmol, 31% excess) and 60 μL of Karstedt catalyst in 50 mL of dry THF. The reaction mixture was stirred and heated to 55 °C for 19 h. Volatiles were removed at reduced pressure, and the resulting tan solid was extracted with 75 mL of hot hexane and filtered through a pad of silica gel. Hexane was removed at reduced pressure, and the white, semicrystalline residue was recrystallized from 100 mL of hot ethanol, giving colorless needles (4.99 g, 52%): mp 83–85 °C; IR (NaCl disk) 2954 (s), 2901 (s), 2881 (s), 2787 (m), 1394 (s), 1248 (s), 1174 (m), 1130 (s), 1104 (m), 1057 (s), 845 (s); <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ -0.079 (s, 12 H, Si(CH<sub>3</sub>)(CH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>), 0.074 (s, 48 H, Si(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>Cl), 0.35 (s, br, 16 H, Si(CH<sub>2</sub>CH<sub>2</sub>)<sub>4</sub>), 0.44 (m, 32 H, SiCH<sub>2</sub>CH<sub>2</sub>SiCH<sub>2</sub>Cl), 2.77 (s, 16 H, CH<sub>2</sub>Cl); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ -6.63 (Si(CH<sub>3</sub>)(CH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>), -5.04 (Si(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>Cl), 2.55 (Si(CH<sub>2</sub>CH<sub>2</sub>)<sub>4</sub>), 4.21 (SiCH<sub>2</sub>CH<sub>2</sub>SiCH<sub>2</sub>Cl), 4.70 (Si(CH<sub>2</sub>CH<sub>2</sub>)<sub>4</sub>), 5.68 (SiCH<sub>2</sub>CH<sub>2</sub>SiCH<sub>2</sub>Cl), 29.93 (CH<sub>2</sub>Cl); <sup>29</sup>Si NMR (CDCl<sub>3</sub>) δ 4.89 (8 Si, SiCH<sub>2</sub>Cl), 7.99 (4 Si, Si(CH<sub>3</sub>)(CH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>), 9.06 (1 Si, Si(CH<sub>2</sub>CH<sub>2</sub>)<sub>4</sub>); GPC *M<sub>w</sub>* = 1310, *M<sub>n</sub>* = 1260 (Calcd *M<sub>n</sub>* = 1398), *D* = 1.04. Anal. Calcd for C<sub>52</sub>H<sub>124</sub>Cl<sub>8</sub>Si<sub>13</sub>: C, 44.67; H, 8.94. Found: C, 45.05; H, 8.83.

**Preparation of 2G-16CH<sub>2</sub>Cl.** The procedure used in the preparation of **OG-4CH<sub>2</sub>Cl** was used in the reaction of 0.512 g of **2G-16Vi** (0.389 mmol) with 1.01 g of (chloromethyl)dimethylsilane (9.28 mmol, 50% excess) and 3 drops of Karstedt catalyst in 20 mL of dry THF. The reaction mixture was stirred and heated to 54 °C for 22 h. All volatiles were removed at reduced pressure, leaving a viscous, brown oil that was purified by flash chromatography (silica gel; 5% ethyl acetate in hexane). Removal of the solvents at reduced pressure and drying for 20 h at room temperature and 0.09 Torr left a clear, colorless, viscous oil (1.08 g, 90%): IR (NaCl disk) 2953 (s), 2903 (s), 2788 (m), 1404 (s), 1248 (s), 1174 (m), 1130 (s), 1104 (m), 1059 (s), 793 (s); <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ -0.082 (s, 36 H, Si(CH<sub>3</sub>)(CH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub> (two types)), 0.078 (s, 96 H, Si(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>Cl), 0.36 (s, br, 48 H, SiCH<sub>2</sub>CH<sub>2</sub>Si(CH<sub>3</sub>)(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub> (two types)), 0.44 (m, 64 H, SiCH<sub>2</sub>CH<sub>2</sub>SiCH<sub>2</sub>Cl), 1.00 (d, *J* = 7.4 Hz, 4.2 H, SiCH(CH<sub>3</sub>)Si), 2.76 (s, 32 H, CH<sub>2</sub>Cl); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ -6.52 (Si(CH<sub>3</sub>)(CH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub> (two types)), -5.03 (Si(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>Cl), 2.42 (br, Si(CH<sub>2</sub>CH<sub>2</sub>)<sub>4</sub>), 4.20 (SiCH<sub>2</sub>CH<sub>2</sub>SiCH<sub>2</sub>Cl), 4.37 (Si(CH<sub>3</sub>)CH<sub>2</sub>CH<sub>2</sub>Si(CH<sub>3</sub>)CH<sub>2</sub>CH<sub>2</sub>SiCH<sub>2</sub>Cl), 4.68 (Si(CH<sub>3</sub>)CH<sub>2</sub>CH<sub>2</sub>Si(CH<sub>3</sub>)CH<sub>2</sub>CH<sub>2</sub>SiCH<sub>2</sub>Cl), 4.84 (Si(CH<sub>2</sub>CH<sub>2</sub>)<sub>4</sub>), 5.69 (SiCH<sub>2</sub>CH<sub>2</sub>SiCH<sub>2</sub>Cl), 29.86 (CH<sub>2</sub>Cl); <sup>29</sup>Si NMR (CDCl<sub>3</sub>) δ 4.32 (16 Si, SiCH<sub>2</sub>Cl); 7.25 (Si(CH<sub>3</sub>)CH<sub>2</sub>CH<sub>2</sub>Si(CH<sub>3</sub>)CH<sub>2</sub>CH<sub>2</sub>SiCH<sub>2</sub>Cl), 7.44 (Si(CH<sub>3</sub>)CH<sub>2</sub>CH<sub>2</sub>SiCH<sub>2</sub>Cl) (overlapped, 12 Si); 9.01 (1 Si, Si(CH<sub>2</sub>CH<sub>2</sub>)<sub>4</sub>); GPC *M<sub>w</sub>* = 2100, *M<sub>n</sub>* = 1940 (Calcd *M<sub>n</sub>* = 3053), *D* = 1.08. Anal. Calcd for C<sub>116</sub>H<sub>276</sub>Cl<sub>16</sub>Si<sub>29</sub>: C, 45.63; H, 9.11. Found: C, 46.10; H, 9.09.

**Preparation of OG-4OH.** A solution of 0.746 g (1.31 mmol) of **OG-4CH<sub>2</sub>Cl** in ca. 25 mL of ethanol was combined with a solution of 0.62 g of NaOH pellets and 0.50 g (6.4 mmol) of 2-mercaptoethanol in 3 mL of distilled water in a 50 mL three-necked, round-bottomed flask equipped with a reflux condenser, magnetic stir bar, and two glass stoppers. This mixture was heated to 80 °C for 6 h. After the mixture was cooled to room temperature and acidified to pH 2 with concentrated HCl(aq), all volatiles were removed at reduced pressure. The residue was extracted with 30 mL of diethyl ether and 30 mL of distilled water. The organic layer was separated, and the aqueous layer was washed with 30 mL of diethyl ether. The combined organic phases were dried

over anhydrous MgSO<sub>4</sub> and filtered. Diethyl ether was removed at reduced pressure, and the residue was dried for 20.5 h at room temperature and 0.1 Torr, giving pure **OG-4OH** as a slightly yellow, crystalline solid (0.943 g, 98%): mp 39–40 °C; IR (NaCl disk) 3356 (br s), 2952 (s), 2905 (s), 2879 (s), 1404 (m), 1247 (s), 1131 (s), 1046 (s), 1009 (m), 845 (vs), 787 (s); <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 0.063 (s, 24 H, CH<sub>3</sub>), 0.43 (s, 16 H, SiCH<sub>2</sub>CH<sub>2</sub>Si), 1.77 (s, 8 H, SiCH<sub>2</sub>S), 2.47 (br s, 4 H, OH), 2.69 (t, *J* = 5.9 Hz, 8 H, SCH<sub>2</sub>CH<sub>2</sub>OH), 3.72 (t, *J* = 5.9 Hz, 8 H, SCH<sub>2</sub>CH<sub>2</sub>OH); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ -4.00 (CH<sub>3</sub>), 2.38 (SiCH<sub>2</sub>CH<sub>2</sub>SiCH<sub>2</sub>S), 6.82 (SiCH<sub>2</sub>CH<sub>2</sub>SiCH<sub>2</sub>S), 15.82 (SiCH<sub>2</sub>S), 39.01 (SCH<sub>2</sub>CH<sub>2</sub>OH), 59.20 (SCH<sub>2</sub>CH<sub>2</sub>OH); <sup>29</sup>Si NMR (CDCl<sub>3</sub>) δ 3.39 (4 Si, SiCH<sub>2</sub>S), 9.30 (1 Si, Si(CH<sub>2</sub>CH<sub>2</sub>)<sub>4</sub>). Anal. Calcd for C<sub>28</sub>H<sub>68</sub>O<sub>4</sub>S<sub>4</sub>Si<sub>5</sub>: C, 45.60; H, 9.29. Found: C, 45.44; H, 9.21.

**Preparation of 1G-8OH.** Following the above procedure, a solution of 0.995 g (0.712 mmol) of **1G-8CH<sub>2</sub>Cl** in ca. 15 mL of 2-propanol was combined with a solution of 0.72 g of NaOH pellets and 0.56 g (7.2 mmol) of 2-mercaptoethanol in 3 mL of distilled water. This mixture was heated to 80 °C for 17 h. The product was purified as in the above procedure and dried for 24 h at room temperature and 0.002 Torr, giving pure **1G-8OH** as a slightly yellow, viscous oil (1.221 g, 99%): IR (NaCl disk) 3355 (br m), 2952 (s), 2904 (s), 2879 (s), 1404 (m), 1248 (s), 1130 (s), 1048 (s), 1011 (s), 838 (vs); <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ -0.099 (s, 12 H, Si(CH<sub>3</sub>)(CH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>), 0.038 (s, 48 H, Si(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>S), 0.33 (br s, 16 H, Si(CH<sub>2</sub>CH<sub>2</sub>)<sub>4</sub>), 0.40 (br s, 32 H, SiCH<sub>2</sub>CH<sub>2</sub>SiCH<sub>2</sub>S), 1.75 (s, 16 H, SiCH<sub>2</sub>S), 2.6 (br, OH), 2.66 (t, *J* = 5.9 Hz, SCH<sub>2</sub>CH<sub>2</sub>OH) (overlapped, 24 H), 3.69 (t, *J* = 5.9 Hz, 16 H, SCH<sub>2</sub>CH<sub>2</sub>OH); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ -6.60 (Si(CH<sub>3</sub>)(CH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>), -3.91 (Si(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>S), 2.46 (Si(CH<sub>2</sub>CH<sub>2</sub>)<sub>4</sub>), 4.27 (SiCH<sub>2</sub>CH<sub>2</sub>SiCH<sub>2</sub>S), 4.70 (Si(CH<sub>2</sub>CH<sub>2</sub>)<sub>4</sub>), 6.97 (SiCH<sub>2</sub>CH<sub>2</sub>SiCH<sub>2</sub>S), 15.78 (SiCH<sub>2</sub>S), 39.06 (SCH<sub>2</sub>CH<sub>2</sub>OH), 59.15 (SCH<sub>2</sub>CH<sub>2</sub>OH); <sup>29</sup>Si NMR (CDCl<sub>3</sub>) δ 3.36 (8 Si, SiCH<sub>2</sub>S), 7.64 (Si(CH<sub>3</sub>)(CH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>), 8.87 (1 Si, Si(CH<sub>2</sub>CH<sub>2</sub>)<sub>4</sub>). Anal. Calcd for C<sub>68</sub>H<sub>164</sub>O<sub>8</sub>S<sub>8</sub>Si<sub>13</sub>: C, 47.17; H, 9.55. Found: C, 47.38; H, 9.23.

**Preparation of OG-4NMe<sub>2</sub>.** The procedure used in the preparation of **OG-4OH** was used in the reaction of 0.51 g (0.88 mmol) of **OG-4CH<sub>2</sub>Cl** with 0.54 g of NaOH pellets and 0.55 g (95% purity, 3.7 mmol) of 2-(dimethylamino)ethanethiol hydrochloride in ca. 25 mL of ethanol and 5 mL of distilled water. This mixture was heated to 80 °C for 9.5 h. The product was purified as in the procedure for the preparation of **OG-4OH**, except that the reaction mixture was not acidified. The residue was dried for 18.5 h at room temperature and 0.01 Torr, giving pure **OG-4NMe<sub>2</sub>** as a slightly yellow, viscous oil (0.76 g, 100%): IR (NaCl disk) 2951 (s), 2905 (s), 2815 (s), 2766 (s), 1458 (s), 1402 (m), 1297 (m), 1247 (vs), 1209 (w), 1166 (m), 1130 (s), 1054 (s), 1042 (s), 1013 (m), 852 (vs); <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 0.047 (s, 24 H, SiCH<sub>3</sub>), 0.41 (s, 16 H, SiCH<sub>2</sub>CH<sub>2</sub>Si), 1.80 (s, 8 H, SiCH<sub>2</sub>S), 2.23 (s, 24 H, NCH<sub>3</sub>), 2.54 (m, 16 H, SCH<sub>2</sub>CH<sub>2</sub>N); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ -3.89 (SiCH<sub>3</sub>), 2.51 (SiCH<sub>2</sub>CH<sub>2</sub>Si), 7.04 (SiCH<sub>2</sub>CH<sub>2</sub>Si), 17.13 (SiCH<sub>2</sub>S), 34.28 (SCH<sub>2</sub>CH<sub>2</sub>N), 45.45 (NCH<sub>3</sub>), 58.99 (SCH<sub>2</sub>CH<sub>2</sub>N); <sup>29</sup>Si NMR (CDCl<sub>3</sub>) δ 3.21 (4 Si, SiCH<sub>2</sub>S), 9.21 (1 Si, Si(CH<sub>2</sub>CH<sub>2</sub>)<sub>4</sub>). Anal. Calcd for C<sub>36</sub>H<sub>88</sub>N<sub>4</sub>S<sub>4</sub>Si<sub>5</sub>: C, 51.12; H, 10.49. Found: C, 51.18; H, 10.97.

**Preparation of 1G-8NMe<sub>2</sub>.** The procedure used in the preparation of **OG-4OH** was used in the reaction of 0.500 g (0.358 mmol) of **1G-8CH<sub>2</sub>Cl** with 0.53 g of NaOH pellets and 0.451 g (95% purity, 3.02 mmol) of 2-(dimethylamino)ethanethiol hydrochloride in ca. 30 mL of 2-propanol and 8 mL of distilled water. This mixture was heated to 85 °C for 11 h. The product was purified as in the above procedure for the synthesis of **OG-4NMe<sub>2</sub>** and dried for 14 h at 85 °C and 0.005 Torr, giving pure **1G-8NMe<sub>2</sub>** as a clear, slightly yellow, viscous oil (0.645 g, 92%): IR (NaCl disk) 2950 (s), 2903 (s), 2815 (s), 2766 (s), 1457 (s), 1403 (m), 1297 (w), 1247 (s), 1130 (s), 1054 (s), 1012 (w), 843 (s); <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ -0.089 (s, 12 H, Si(CH<sub>3</sub>)(CH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>), 0.043 (s, 48 H, Si(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>S), 0.32 (s, 16 H, Si(CH<sub>2</sub>CH<sub>2</sub>)<sub>4</sub>), 0.41 (s, 32 H, SiCH<sub>2</sub>CH<sub>2</sub>SiCH<sub>2</sub>S), 1.79 (s, 16 H, SiCH<sub>2</sub>S), 2.23 (s, 48 H, NCH<sub>3</sub>), 2.54 (m, 32 H, SCH<sub>2</sub>CH<sub>2</sub>N); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ -6.60 (Si(CH<sub>3</sub>)(CH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>), -3.88 (Si(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>S), 2.50 (Si(CH<sub>2</sub>CH<sub>2</sub>)<sub>4</sub>), 4.29 (SiCH<sub>2</sub>CH<sub>2</sub>SiCH<sub>2</sub>S), 4.77 (Si(CH<sub>2</sub>CH<sub>2</sub>)<sub>4</sub>), 7.09 (SiCH<sub>2</sub>CH<sub>2</sub>SiCH<sub>2</sub>S), 17.10 (SiCH<sub>2</sub>S), 34.17 (SCH<sub>2</sub>CH<sub>2</sub>N), 45.37 (NCH<sub>3</sub>), 58.94 (SCH<sub>2</sub>CH<sub>2</sub>N); <sup>29</sup>Si NMR (CDCl<sub>3</sub>) δ 3.20 (8 Si, SiCH<sub>2</sub>S), 7.67 (4 Si, Si(CH<sub>3</sub>)(CH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>), 8.96 (1 Si, Si(CH<sub>2</sub>CH<sub>2</sub>)<sub>4</sub>). Anal. Calcd for C<sub>84</sub>H<sub>204</sub>N<sub>8</sub>S<sub>8</sub>Si<sub>13</sub>: C, 51.79; H, 10.55. Found: C, 51.36; H, 10.36.

**Preparation of 2G-16NMe<sub>2</sub>.** The procedure used in the preparation of **OG-4OH** was used in the reaction of 0.254 g (0.0831 mmol) of **2G-16CH<sub>2</sub>Cl** with 0.22 g of NaOH pellets and 0.21 g (95% purity, 1.5 mmol) of 2-(dimethylamino)ethanethiol hydrochloride in ca. 25 mL of 2-propanol and 1 mL of distilled water. This mixture was heated to reflux for 8.75 h. The product was purified as in the above procedure for the synthesis of **OG-4NMe<sub>2</sub>** and dried for 18 h at 70 °C and 0.002 Torr, giving pure **2G-16NMe<sub>2</sub>** as a clear, slightly yellow, viscous oil (0.318 g, 92%): IR (NaCl disk) 2950 (s), 2903 (s), 2815 (s), 2766 (s), 1457 (s), 1404 (m), 1297 (w), 1247 (s), 1130 (s), 1055 (s), 1013 (w), 850 (s); <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ -0.098 (s, 36 H, Si(CH<sub>3</sub>)(CH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub> (two types)), 0.045 (s, 96 H, Si(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>S), 0.34 (br s, 48 H, SiCH<sub>2</sub>CH<sub>2</sub>-Si(CH<sub>3</sub>)(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub> (two types)), 0.41 (br s, 64 H, SiCH<sub>2</sub>CH<sub>2</sub>SiCH<sub>2</sub>S), 1.00 (d, *J* = 8 Hz, 4.2 H, SiCH(CH<sub>3</sub>)Si), 1.79 (s, 32 H, SiCH<sub>2</sub>S), 2.24 (s, 96 H, NCH<sub>3</sub>), 2.55 (m, 64 H, SCH<sub>2</sub>CH<sub>2</sub>N); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ -6.44 (Si(CH<sub>3</sub>)(CH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub> (two types)), -3.85 (Si(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>S), 2.50 (br, Si(CH<sub>2</sub>CH<sub>2</sub>)<sub>4</sub>), 4.31 (SiCH<sub>2</sub>CH<sub>2</sub>SiCH<sub>2</sub>S), 4.78 (Si(CH<sub>2</sub>CH<sub>2</sub>)<sub>4</sub>, Si-(CH<sub>3</sub>)CH<sub>2</sub>CH<sub>2</sub>Si(CH<sub>3</sub>)CH<sub>2</sub>CH<sub>2</sub>SiCH<sub>2</sub>S), 7.04 (SiCH<sub>2</sub>CH<sub>2</sub>SiCH<sub>2</sub>S), 17.10 (SiCH<sub>2</sub>S), 34.20 (SCH<sub>2</sub>CH<sub>2</sub>N), 45.37 (NCH<sub>3</sub>), 58.93 (SCH<sub>2</sub>CH<sub>2</sub>N); <sup>29</sup>Si NMR (CDCl<sub>3</sub>) δ 3.18 (16 Si, SiCH<sub>2</sub>S), 7.67 (12 Si, Si(CH<sub>3</sub>)(CH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub> (two types)), 9.26 (1 Si, Si(CH<sub>2</sub>CH<sub>2</sub>)<sub>4</sub>). Anal. Calcd for C<sub>180</sub>H<sub>436</sub>N<sub>16</sub>S<sub>16</sub>Si<sub>29</sub>: C, 52.06; H, 10.58. Found: C, 52.49; H, 10.54.

**Preparation of OG-4SO<sub>3</sub>Na.** The procedure used in the preparation of **OG-4OH** was used in the reaction of 0.50 g (0.87 mmol) of **OG-4CH<sub>2</sub>Cl** with 0.28 g of NaOH pellets and 0.70 g (90% purity, 3.7 mmol) of sodium 3-mercaptopropanesulfonate in ca. 25 mL of ethanol and 8 mL of distilled water. This mixture was heated to 80 °C for 6 h and then warmed to reflux for an additional 10 h. Upon cooling to room temperature, a white solid precipitated, which was collected by suction filtration and dried at room temperature and 0.01 Torr for 10 h (mass 0.98 g). A solution of 0.203 g of this solid dissolved in ca. 4 mL of deionized water was acidified to pH 6–7 with 1 M HCl(aq) and placed into a dialysis membrane (MWCO = 500) that was immersed in 65 mL of stirred deionized water for 9.5 h. Evaporation of the contents of the dialysis membrane and drying 48 h at room temperature and 0.005 Torr left **OG-4SO<sub>3</sub>Na** as a white, hygroscopic solid (0.165 g, 80%): IR (KBr pellet) 3437 (s, br), 2954 (s), 2905 (s), 2878 (s), 1640 (w, br), 1456 (w), 1410 (w), 1245 (s), 1194 (vs), 1129 (s), 1058 (s), 842 (s), 779 (m), 734 (s), 612 (m), 532 (m); <sup>1</sup>H NMR (D<sub>2</sub>O) δ 0.15 (s, 24 H, CH<sub>3</sub>), 0.56 (s, 16 H, SiCH<sub>2</sub>CH<sub>2</sub>Si), 1.93 (s, 8 H, SiCH<sub>2</sub>S), 2.06 (m, 8 H, SCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>SO<sub>3</sub>Na), 2.71 (t, *J* = 7.7 Hz, 8 H, SCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-SO<sub>3</sub>Na), 2.99 (m, 8 H, SCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>SO<sub>3</sub>Na); <sup>13</sup>C NMR (D<sub>2</sub>O) δ -3.78 (CH<sub>3</sub>), 2.45 (SiCH<sub>2</sub>CH<sub>2</sub>Si), 6.78 (SiCH<sub>2</sub>CH<sub>2</sub>Si), 15.98 (SiCH<sub>2</sub>S), 23.79 (SCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>SO<sub>3</sub>Na), 34.53 (SCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>SO<sub>3</sub>Na), 50.14 (SCH<sub>2</sub>-CH<sub>2</sub>CH<sub>2</sub>SO<sub>3</sub>Na); <sup>29</sup>Si NMR (D<sub>2</sub>O) δ 3.17 (4 Si, SiCH<sub>2</sub>S), 9.69 (1 Si, Si(CH<sub>2</sub>CH<sub>2</sub>)<sub>4</sub>). Anal. Calcd for C<sub>32</sub>H<sub>72</sub>O<sub>12</sub>S<sub>8</sub>Si<sub>5</sub>·3H<sub>2</sub>O: C, 32.25; H, 6.60. Found: C, 32.43; H, 6.80.

**Preparation of 1G-8SO<sub>3</sub>Na.** The procedure used in the preparation of **OG-4OH** was used in the reaction of 0.594 g (0.425 mmol) of **1G-8CH<sub>2</sub>Cl** with 0.22 g of NaOH pellets and 0.630 g (90% purity, 3.54 mmol) of sodium 3-mercaptopropanesulfonate in ca. 25 mL of 2-propanol and 3 mL of distilled water. This mixture was heated to 95 °C for 15 h. After all volatiles were removed under reduced pressure, the residue was washed once with 25 mL of hot 2-propanol. Deionized water (ca. 6 mL) was added, and the suspension was acidified to pH 6 with 1 M HCl(aq). After solids were removed by centrifugation, the supernate was dialyzed in a MWCO = 100 membrane for 23 h, changing the water once after 13 h. The contents of the dialysis tubing were collected, evaporated at reduced pressure, and dried at 70 °C and 0.05 Torr for 19 h to give **1G-8SO<sub>3</sub>Na** as a hygroscopic, white solid (0.715 g, 66%): IR (KBr pellet) 3456 (s, br), 2951 (m), 2904 (m), 2879 (m), 1650 (m, br), 1452 (s, br), 1248 (s), 1191 (vs), 1130 (s), 1057 (s), 843 (s); <sup>1</sup>H NMR (D<sub>2</sub>O) δ 0.012 (s, 12 H, Si(CH<sub>3</sub>)(CH<sub>2</sub>-CH<sub>2</sub>)<sub>3</sub>), 0.13 (s, 48 H, Si(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>S), 0.49 (s, 16 H, Si(CH<sub>2</sub>CH<sub>2</sub>)<sub>4</sub>), 0.53 (s, 32 H, SiCH<sub>2</sub>CH<sub>2</sub>SiCH<sub>2</sub>S), 1.90 (s, 16 H, SiCH<sub>2</sub>S), 2.06 (m, 16 H, SCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>SO<sub>3</sub>Na), 2.68 (t, *J* = 7.7 Hz, 8 H, SCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-SO<sub>3</sub>Na), 2.99 (m, 8 H, SCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>SO<sub>3</sub>Na); <sup>13</sup>C NMR (D<sub>2</sub>O) δ -5.93 (Si(CH<sub>3</sub>)(CH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>), -3.73 (Si(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>S), 2.90 (br, Si(CH<sub>2</sub>CH<sub>2</sub>)<sub>4</sub>), 4.39 (SiCH<sub>2</sub>CH<sub>2</sub>SiCH<sub>2</sub>S), 4.71 (Si(CH<sub>2</sub>CH<sub>2</sub>)<sub>4</sub>), 7.06 (SiCH<sub>2</sub>CH<sub>2</sub>SiCH<sub>2</sub>S), 16.09 (SiCH<sub>2</sub>S), 23.85 (SCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>SO<sub>3</sub>Na), 34.59 (SCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-SO<sub>3</sub>Na), 50.09 (SCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>SO<sub>3</sub>Na); <sup>29</sup>Si NMR (D<sub>2</sub>O) δ 2.84 (8 Si,

SiCH<sub>2</sub>S), 7.29 (4 Si, Si(CH<sub>3</sub>)(CH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>), 8.88 (1 Si, Si(CH<sub>2</sub>CH<sub>2</sub>)<sub>4</sub>). Anal. Calcd for C<sub>76</sub>H<sub>172</sub>Na<sub>8</sub>O<sub>24</sub>S<sub>16</sub>Si<sub>13</sub> + 2.43NaCl: C, 34.13; H, 6.49; Cl, 3.23. Found: C, 33.72; H, 6.35; total halogen (Calcd as Cl), 3.23.

**Preparation of 2G-16SO<sub>3</sub>Na.** The procedure used in the preparation of **OG-4OH** was used in the reaction of 0.252 g (0.082 mmol) of **2G-16CH<sub>2</sub>Cl** with 0.1 g of NaOH pellets and 0.260 g (90% purity, 1.31 mmol) of sodium 3-mercaptopropanesulfonate in ca. 20 mL of 2-propanol and 3 mL of distilled water. This mixture was heated to reflux for 4 h. The crude product was purified as in the above example for the preparation of **1G-8SO<sub>3</sub>Na** (except that a MWCO = 500 dialysis membrane was used) and dried at 48 °C and 0.03 Torr for 19.75 h, yielding **2G-16SO<sub>3</sub>Na** as a hygroscopic, white solid (0.328 g, 75%): IR (KBr pellet) 3456 (s, br), 2951 (s), 2904 (s), 2879 (m), 1636 (m, br), 1406 (m, br), 1248 (s), 1194 (s, br, *ν*<sub>as</sub> SO<sub>3</sub>), 1131 (s), 1055 (s, *ν*<sub>s</sub> SO<sub>3</sub>), 795 (s, br), 610 (m), 530 (m); <sup>1</sup>H NMR (D<sub>2</sub>O) δ 0.047 (br s, Si(CH<sub>3</sub>)(CH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub> (two types)), 0.17 (br s, Si(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>S) (overlapped, 132 H), 0.55 (br, 112 H, SiCH<sub>2</sub>CH<sub>2</sub>Si), 1.00 (d, *J* = 8 Hz, 4.2 H, SiCH-(CH<sub>3</sub>)Si), 1.93 (s, 32 H, SiCH<sub>2</sub>S), 2.09 (pent, *J* = 7.3 Hz, 32 H, SCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>SO<sub>3</sub>Na), 2.72 (t, *J* = 6.5 Hz, 32 H, SCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>SO<sub>3</sub>-Na), 3.03 (t, *J* = 7.6 Hz, 32 H, SCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>SO<sub>3</sub>Na); <sup>13</sup>C NMR (D<sub>2</sub>O) δ -5.88 (Si(CH<sub>3</sub>)(CH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub> (two types)), -3.71 (Si(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>S), 4.38 (br, SiCH<sub>2</sub>CH<sub>2</sub>SiCH<sub>2</sub>S, Si(CH<sub>3</sub>)CH<sub>2</sub>CH<sub>2</sub>Si(CH<sub>3</sub>)CH<sub>2</sub>CH<sub>2</sub>SiCH<sub>2</sub>S), 5.2 (SiCH<sub>2</sub>CH<sub>2</sub>Si(CH<sub>3</sub>)(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub> (two types)), 7.00 (SiCH<sub>2</sub>CH<sub>2</sub>SiCH<sub>2</sub>S), 16.05 (SiCH<sub>2</sub>S), 23.87 (SCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>SO<sub>3</sub>Na), 34.61 (SCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-SO<sub>3</sub>Na), 50.17 (SCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>SO<sub>3</sub>Na); <sup>29</sup>Si NMR (D<sub>2</sub>O) δ 3.14 (16 Si, SiCH<sub>2</sub>S), 7.44 (Si(CH<sub>2</sub>CH<sub>2</sub>SiCH<sub>3</sub>)<sub>4</sub>), 7.66 (Si(CH<sub>3</sub>)CH<sub>2</sub>CH<sub>2</sub>SiCH<sub>2</sub>S), 8.23 (Si(CH<sub>2</sub>CH<sub>2</sub>)<sub>4</sub>) (overlapped, 13 Si). Anal. Calcd for C<sub>164</sub>H<sub>372</sub>-Na<sub>16</sub>O<sub>48</sub>S<sub>32</sub>Si<sub>29</sub>·6H<sub>2</sub>O: C, 36.28; H, 7.13. Found: C, 36.44; H, 7.18.

**Preparation of OG-4NMe<sub>2</sub>HCl.** A solution of 0.205 g (0.242 mmol) of **OG-4NMe<sub>2</sub>** in 60 mL of diethyl ether was shaken vigorously with ca. 50 mL of 1 M HCl(aq) in a separatory funnel. The aqueous layer was separated, the water was removed under reduced pressure, and the residue was dried at room temperature and 0.01 Torr for 63.5 h, leaving **OG-4NMe<sub>2</sub>HCl** as a white crystalline solid (0.238 g, 99%): mp 237–8 °C dec; <sup>1</sup>H NMR (D<sub>2</sub>O) δ -0.094 (s, 24 H, SiCH<sub>3</sub>), 0.53 (s, 16 H, SiCH<sub>2</sub>CH<sub>2</sub>Si), 1.97 (s, 8 H, SiCH<sub>2</sub>S), 2.92 (s, m; 32 H, NCH<sub>3</sub>, SCH<sub>2</sub>CH<sub>2</sub>N), 3.40 (t, *J* = 7.3 Hz, 8 H, SCH<sub>2</sub>CH<sub>2</sub>N); <sup>13</sup>C NMR (D<sub>2</sub>O) δ -4.00 (SiCH<sub>3</sub>), 2.33 (SiCH<sub>2</sub>CH<sub>2</sub>Si), 6.60 (SiCH<sub>2</sub>CH<sub>2</sub>Si), 15.76 (SiCH<sub>2</sub>S), 29.49 (SCH<sub>2</sub>CH<sub>2</sub>N), 42.88 (NCH<sub>3</sub>), 56.05 (SCH<sub>2</sub>CH<sub>2</sub>N); <sup>29</sup>Si NMR (D<sub>2</sub>O) δ 3.34 (4 Si, SiCH<sub>2</sub>S), 9.57 (1 Si, Si(CH<sub>2</sub>CH<sub>2</sub>)<sub>4</sub>).

**Preparation of 1G-8NMe<sub>2</sub>HCl.** The above procedure for the preparation of **OG-4NMe<sub>2</sub>HCl** was followed, using 0.222 g (0.159 mmol) of **1G-8NMe<sub>2</sub>** and 10 mL of 1 M HCl(aq). Drying the product for 18 h at room temperature and 0.01 Torr gave **1G-8NMe<sub>2</sub>HCl** as a white tacky solid (0.266 g, 75%): <sup>1</sup>H NMR (D<sub>2</sub>O) δ 0.02 (br s, 12 H, Si(CH<sub>3</sub>)(CH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>), 0.16 (br s, 48 H, Si(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>S), 0.47 (br s, 16 H, Si(CH<sub>2</sub>CH<sub>2</sub>)<sub>4</sub>), 0.52 (br s, 32 H, SiCH<sub>2</sub>CH<sub>2</sub>SiCH<sub>2</sub>S), 2.00 (br s, 16 H, SiCH<sub>2</sub>S), 2.96 (br; 64 H; SCH<sub>2</sub>CH<sub>2</sub>N, NCH<sub>3</sub>), 3.42 (br m, 16 H, SCH<sub>2</sub>CH<sub>2</sub>N); <sup>13</sup>C NMR (D<sub>2</sub>O) δ -5.85 (Si(CH<sub>3</sub>)(CH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>), -3.62, -3.58 (Si(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>S), 2.35 (br, Si(CH<sub>2</sub>CH<sub>2</sub>)<sub>4</sub>), 4.38 (br, SiCH<sub>2</sub>CH<sub>2</sub>-SiCH<sub>2</sub>S), 4.75 (br, Si(CH<sub>2</sub>CH<sub>2</sub>)<sub>4</sub>), 6.94 (SiCH<sub>2</sub>CH<sub>2</sub>SiCH<sub>2</sub>S), 16.03 (SiCH<sub>2</sub>S), 29.61 (SCH<sub>2</sub>CH<sub>2</sub>N), 43.00 (NCH<sub>3</sub>), 56.22 (SCH<sub>2</sub>CH<sub>2</sub>N); <sup>29</sup>Si NMR (D<sub>2</sub>O) δ 3.06 (8 Si, SiCH<sub>2</sub>S), 7.31 (4 Si, Si(CH<sub>3</sub>)(CH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>), 8.66 (1 Si, Si(CH<sub>2</sub>CH<sub>2</sub>)<sub>4</sub>).

**Preparation of 2G-16NMe<sub>2</sub>HCl.** The above procedure for the preparation of **OG-4NMe<sub>2</sub>HCl** was followed, using 0.144 g (0.035 mmol) of **2G-16NMe<sub>2</sub>** and 20 mL of 1 M HCl(aq). Drying the product for 18 h at 50 °C and 0.005 Torr gave **2G-16NMe<sub>2</sub>HCl** as a white tacky solid (0.162 g, 99%): <sup>1</sup>H NMR (D<sub>2</sub>O) δ 0.016 (br, 36 H, Si(CH<sub>3</sub>)(CH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub> (two types)), 0.16 (br s, 96 H, Si(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>S), 0.45 (br, SiCH<sub>2</sub>CH<sub>2</sub>Si(CH<sub>3</sub>)(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub> (two types)), 0.53 (br, SiCH<sub>2</sub>CH<sub>2</sub>-SiCH<sub>2</sub>S) (overlapped, 112 H), 1.0 (d, *J* = 7 Hz, 4.2 H, SiCH(CH<sub>3</sub>)Si), 2.02 (br s, 32 H, SiCH<sub>2</sub>S), 2.98 (br, 128 H, SCH<sub>2</sub>CH<sub>2</sub>N, NCH<sub>3</sub>), 3.44 (br m, 32 H, SCH<sub>2</sub>CH<sub>2</sub>N); <sup>13</sup>C NMR (D<sub>2</sub>O) δ -5.96 (Si(CH<sub>3</sub>)(CH<sub>2</sub>-CH<sub>2</sub>)<sub>3</sub> (two types)), -3.69 (Si(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>S), 4.27 (SiCH<sub>2</sub>CH<sub>2</sub>SiCH<sub>2</sub>S), 5.0 (Si(CH<sub>2</sub>CH<sub>2</sub>)<sub>4</sub>), Si(CH<sub>3</sub>)CH<sub>2</sub>CH<sub>2</sub>Si(CH<sub>3</sub>)CH<sub>2</sub>CH<sub>2</sub>SiCH<sub>2</sub>S), 6.82 (SiCH<sub>2</sub>CH<sub>2</sub>SiCH<sub>2</sub>S), 15.91 (SiCH<sub>2</sub>S), 29.50 (SCH<sub>2</sub>CH<sub>2</sub>N), 42.92 (NCH<sub>3</sub>), 56.12 (SCH<sub>2</sub>CH<sub>2</sub>N); <sup>29</sup>Si NMR (D<sub>2</sub>O) δ 3.34 (16 Si, SiCH<sub>2</sub>S), 7.5



(Si(CH<sub>2</sub>CH<sub>2</sub>SiCH<sub>3</sub>)<sub>4</sub>), 7.68 (Si(CH<sub>3</sub>)CH<sub>2</sub>CH<sub>2</sub>SiCH<sub>2</sub>S) (overlapped, 12 Si), 9.26 (1 Si, Si(CH<sub>2</sub>CH<sub>2</sub>)<sub>4</sub>).

**Preparation of OG-4NMe<sub>3</sub>I.** In a 50 mL three-necked, round-bottomed flask equipped with a reflux condenser, magnetic stir bar, and two glass stoppers were combined 0.223 g (0.264 mmol) of **OG-4NMe<sub>2</sub>**, ca. 25 mL of absolute ethanol, and 0.10 mL (0.23 g, 1.6 mmol) of methyl iodide. The reaction mixture was heated to reflux in an oil bath for 3.5 h. After the mixture was cooled to room temperature, ca. 20 mL of anhydrous diethyl ether was added to precipitate the quaternary ammonium salt. The precipitate was collected by suction filtration, washed twice with 5 mL portions of ether, and dried for 21 h at room temperature and 0.005 Torr, giving **OG-4NMe<sub>3</sub>I** as a fine, white solid (0.372 g, 99%): <sup>1</sup>H NMR (CD<sub>3</sub>OD) δ 0.14 (s, 24 H, SiCH<sub>3</sub>), 0.57 (s, 16 H, SiCH<sub>2</sub>CH<sub>2</sub>Si), 2.13 (s + sh, 8 H, SiCH<sub>2</sub>S), 3.03 (m, 8 H, SCH<sub>2</sub>CH<sub>2</sub>N), 3.28 (s + 2 sh, 36 H, NCH<sub>3</sub>), 3.76 (m, 8 H, SCH<sub>2</sub>CH<sub>2</sub>N); <sup>13</sup>C NMR (CD<sub>3</sub>OD) δ -3.54 (SiCH<sub>3</sub>), 3.85 (SiCH<sub>2</sub>CH<sub>2</sub>Si), 8.30 (SiCH<sub>2</sub>CH<sub>2</sub>Si), 17.97 (SiCH<sub>2</sub>S), 29.47 (SCH<sub>2</sub>CH<sub>2</sub>N), 54.11 (t + sh, J<sub>N-C</sub> = 4.2 Hz, NCH<sub>3</sub>), 66.90 (SCH<sub>2</sub>CH<sub>2</sub>N); <sup>29</sup>Si NMR (CD<sub>3</sub>OD) δ 4.10 (4 Si, SiCH<sub>2</sub>S), 9.74 (1 Si, Si(CH<sub>2</sub>CH<sub>2</sub>)<sub>4</sub>). Anal. Calcd for C<sub>40</sub>H<sub>100</sub>Cl<sub>4</sub>N<sub>4</sub>S<sub>4</sub>Si<sub>5</sub>: C, 33.99; H, 7.13. Found: C, 33.51; H, 7.20.

**Preparation of 1G-8NMe<sub>3</sub>I.** The above procedure for the preparation of **OG-4NMe<sub>3</sub>I** was followed, using 0.622 g (0.319 mmol) of **1G-8NMe<sub>2</sub>** and 0.20 mL (0.46 g, 3.2 mmol) of MeI. The product was dried at room temperature and 0.003 Torr for 20 h, giving **1G-8NMe<sub>3</sub>I** as a white powder (0.945 g, 96%): <sup>1</sup>H NMR (CD<sub>3</sub>OD) δ -0.027 (s, 12 H, Si(CH<sub>3</sub>)(CH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>), 0.10 (s, 48 H, Si(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>S), 0.43 (br s, 16 H, Si(CH<sub>2</sub>CH<sub>2</sub>)<sub>4</sub>), 0.52 (br s, 32 H, SiCH<sub>2</sub>CH<sub>2</sub>SiCH<sub>2</sub>S), 2.07 (s + sh, 16 H, SiCH<sub>2</sub>S), 2.97 (m, 16 H, SCH<sub>2</sub>CH<sub>2</sub>N), 3.22 (s, 72 H, NCH<sub>3</sub>), 3.69 (m, 16 H, SCH<sub>2</sub>CH<sub>2</sub>N); <sup>13</sup>C NMR (CD<sub>3</sub>OD) δ -5.93 (Si(CH<sub>3</sub>)(CH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>), -3.33 (Si(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>S), 3.61 (Si(CH<sub>2</sub>CH<sub>2</sub>)<sub>4</sub>), 5.50 (SiCH<sub>2</sub>CH<sub>2</sub>SiCH<sub>2</sub>S), 5.82 (Si(CH<sub>2</sub>CH<sub>2</sub>)<sub>4</sub>), 8.26 (SiCH<sub>2</sub>CH<sub>2</sub>SiCH<sub>2</sub>S), 17.74 (SiCH<sub>2</sub>S), 29.40 (SCH<sub>2</sub>CH<sub>2</sub>N), 54.05 (t, J<sub>N-C</sub> = 3.5 Hz, NCH<sub>3</sub>), 66.72 (SCH<sub>2</sub>CH<sub>2</sub>N); <sup>29</sup>Si NMR (CD<sub>3</sub>OD) δ 4.10 (8 Si, SiCH<sub>2</sub>S), 8.14 (4 Si, Si(CH<sub>3</sub>)(CH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>), 9.52 (1 Si, Si(CH<sub>2</sub>CH<sub>2</sub>)<sub>4</sub>). Anal. Calcd for C<sub>92</sub>H<sub>228</sub>I<sub>8</sub>N<sub>8</sub>S<sub>8</sub>Si<sub>13</sub>: C, 35.83; H, 7.45. Found: C, 35.93; H, 7.55.

**Preparation of 2G-16NMe<sub>3</sub>I.** The above procedure for the preparation of **OG-4NMe<sub>3</sub>I** was followed, using 0.226 g (0.054 mmol) of **2G-16NMe<sub>2</sub>** and 0.10 mL (0.23 g, 1.6 mmol) of MeI. The product was dried at room temperature and 0.02 Torr for 14.5 h, giving **2G-16NMe<sub>3</sub>I** as a white powder (0.309 g, 89%): <sup>1</sup>H NMR (CD<sub>3</sub>OD) δ 0.053 (br, 36 H, Si(CH<sub>3</sub>)(CH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub> (two types)), 0.19 (s, 96 H, Si(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>S), 0.50 (br s, 48 H, SiCH<sub>2</sub>CH<sub>2</sub>Si(CH<sub>3</sub>)(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub> (two types)), 0.59 (br s, 16 H, SiCH<sub>2</sub>CH<sub>2</sub>Si(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>S), 1.0 (d, J = 8 Hz, 4.2 H, SiCH(CH<sub>3</sub>)Si), 2.19 (s, 32 H, SiCH<sub>2</sub>S), 3.08 (m, 32 H, SCH<sub>2</sub>CH<sub>2</sub>N), 3.37 (br s, 144 H, NCH<sub>3</sub>), 3.84 (m, 32 H, SCH<sub>2</sub>CH<sub>2</sub>N); <sup>13</sup>C NMR (CD<sub>3</sub>OD) δ -5.33 (Si(CH<sub>3</sub>)(CH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub> (two types)), -2.91 (Si(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>S), 3.7 (br, Si(CH<sub>2</sub>CH<sub>2</sub>)<sub>4</sub>), 5.72 (SiCH<sub>2</sub>CH<sub>2</sub>SiCH<sub>2</sub>S), 6.06 (br, Si(CH<sub>2</sub>CH<sub>2</sub>)<sub>4</sub>), Si(CH<sub>3</sub>)CH<sub>2</sub>CH<sub>2</sub>Si(CH<sub>3</sub>)CH<sub>2</sub>CH<sub>2</sub>SiCH<sub>2</sub>S), 8.44 (SiCH<sub>2</sub>CH<sub>2</sub>SiCH<sub>2</sub>S), 18.02 (SiCH<sub>2</sub>S), 29.67 (SCH<sub>2</sub>CH<sub>2</sub>N), 54.34 (t, J<sub>N-C</sub> = 4.6 Hz, NCH<sub>3</sub>), 66.90 (SCH<sub>2</sub>CH<sub>2</sub>N); <sup>29</sup>Si NMR (CD<sub>3</sub>OD) δ 4.04 (16 Si, SiCH<sub>2</sub>S), 8.00 (Si(CH<sub>2</sub>CH<sub>2</sub>SiCH<sub>3</sub>)<sub>4</sub>), 8.18 (Si(CH<sub>3</sub>)CH<sub>2</sub>CH<sub>2</sub>SiCH<sub>2</sub>S) (overlapped, 12 Si), 8.77 (1 Si, Si(CH<sub>2</sub>CH<sub>2</sub>)<sub>4</sub>). Anal. Calcd for C<sub>196</sub>H<sub>484</sub>I<sub>16</sub>N<sub>16</sub>S<sub>16</sub>Si<sub>29</sub>: C, 36.65; H, 7.59. Found: C, 36.62; H, 7.63.

**Preparation of OG-4NMe<sub>3</sub>Cl.** A suspension of 0.134 g of **OG-4NMe<sub>3</sub>I** (0.095 mmol) and 0.193 g (1.35 mmol) of AgCl in ca. 15 mL of deionized water was heated to 65 °C for 4 h in a 25 mL round-bottomed flask equipped with a magnetic stir bar. After the mixture was cooled to room temperature, solids were removed by filtration followed by centrifugation. Water was removed at reduced pressure, leaving a brown solid (0.107 g). Addition of ca. 6 mL of deionized water to this solid formed a suspension that was centrifuged once more. The centrifugate was decanted from the solids, and water was removed at reduced pressure. Drying for 18 h at 55 °C and 0.01 Torr left **OG-4NMe<sub>3</sub>Cl** as a hygroscopic, colorless solid (0.097 g, 97%): <sup>1</sup>H NMR (D<sub>2</sub>O) δ 0.10 (s, 24 H, SiCH<sub>3</sub>), 0.53 (s, 16 H, SiCH<sub>2</sub>CH<sub>2</sub>Si), 2.01 (s, 8 H, SiCH<sub>2</sub>S), 2.98 (m, 8 H, SCH<sub>2</sub>CH<sub>2</sub>N), 3.17 (s + sh, 36 H, NCH<sub>3</sub>), 3.58 (m, 8 H, SCH<sub>2</sub>CH<sub>2</sub>N); <sup>13</sup>C NMR (D<sub>2</sub>O) δ -4.01 (SiCH<sub>3</sub>), 2.35 (SiCH<sub>2</sub>CH<sub>2</sub>Si), 6.57 (SiCH<sub>2</sub>CH<sub>2</sub>Si), 16.12 (SiCH<sub>2</sub>S), 27.87 (SCH<sub>2</sub>CH<sub>2</sub>N), 53.08 (t, J<sub>N-C</sub> = 3.3 Hz, NCH<sub>3</sub>), 65.15 (SCH<sub>2</sub>CH<sub>2</sub>N); <sup>29</sup>Si NMR (D<sub>2</sub>O) δ 3.27 (4 Si, SiCH<sub>2</sub>S), 9.56 (1 Si, Si(CH<sub>2</sub>CH<sub>2</sub>)<sub>4</sub>). Anal. Calcd

for C<sub>40</sub>H<sub>100</sub>Cl<sub>4</sub>N<sub>4</sub>S<sub>4</sub>Si<sub>5</sub>·2H<sub>2</sub>O: C, 44.33; H, 9.67; Cl, 13.08. Found: C, 43.97; H, 9.87; total halogen (Calcd as Cl), 13.28.

**Preparation of 1G-8NMe<sub>3</sub>Cl.** The above procedure for the preparation of **OG-4NMe<sub>3</sub>Cl** was followed, using 0.945 g (0.307 mmol) of **1G-8NMe<sub>3</sub>I** and 1.44 g (10.0 mmol) of AgCl. After the product was dried for 24 h at 60 °C and 0.003 Torr, **1G-8NMe<sub>3</sub>Cl** was obtained as a slightly yellow solid (0.704 g, 98%): <sup>1</sup>H NMR (D<sub>2</sub>O) δ 0.031 (br s, 12 H, Si(CH<sub>3</sub>)(CH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>), 0.18 (s, 48 H, Si(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>S), 0.48 (br s, Si(CH<sub>2</sub>CH<sub>2</sub>)<sub>4</sub>), 0.54 (br s, SiCH<sub>2</sub>CH<sub>2</sub>SiCH<sub>2</sub>S) (overlapped, 48 H), 2.07 (s, 16 H, SiCH<sub>2</sub>S), 3.01 (m, 4 H, SCH<sub>2</sub>CH<sub>2</sub>N), 3.24 (s + sh, 72 H, NCH<sub>3</sub>), 3.64 (m, 16 H, SCH<sub>2</sub>CH<sub>2</sub>N); <sup>13</sup>C NMR (D<sub>2</sub>O) δ -6.34 (Si(CH<sub>3</sub>)(CH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>), -4.21, -4.11 (Si(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>S), 2.34 (br, Si(CH<sub>2</sub>CH<sub>2</sub>)<sub>4</sub>), 3.90 (SiCH<sub>2</sub>CH<sub>2</sub>SiCH<sub>2</sub>S), 4.30 (br, Si(CH<sub>2</sub>CH<sub>2</sub>)<sub>4</sub>), 6.39 (SiCH<sub>2</sub>CH<sub>2</sub>SiCH<sub>2</sub>S), 15.83 (SiCH<sub>2</sub>S), 27.58 (SCH<sub>2</sub>CH<sub>2</sub>N), 52.76 (NCH<sub>3</sub>), 64.79 (SCH<sub>2</sub>CH<sub>2</sub>N); <sup>29</sup>Si NMR (D<sub>2</sub>O) δ 3.32 (8 Si, SiCH<sub>2</sub>S), 7.57 (4 Si, Si(CH<sub>3</sub>)(CH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>), 8.75 (1 Si, Si(CH<sub>2</sub>CH<sub>2</sub>)<sub>4</sub>). Anal. Calcd for C<sub>92</sub>H<sub>228</sub>Cl<sub>8</sub>N<sub>8</sub>S<sub>8</sub>Si<sub>13</sub>: Cl, 12.06. Found: total halogen (Calcd as Cl), 11.55%.

**Preparation of 2G-16NMe<sub>3</sub>Cl.** The above procedure for the preparation of **OG-4NMe<sub>3</sub>Cl** was followed, using 0.157 g (0.0244 mmol) of **2G-16NMe<sub>3</sub>I** and 0.206 g (1.43 mmol) of AgCl. After the product was dried for 19.75 h at 60 °C and 0.04 Torr, **2G-16NMe<sub>3</sub>Cl** was obtained as a colorless solid (0.115 g, 95%): <sup>1</sup>H NMR (D<sub>2</sub>O) δ 0.059 (br, 36 H, Si(CH<sub>3</sub>)(CH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub> (two types)), 0.20 (s, 96 H, Si(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>S), 0.48 (br s, SiCH<sub>2</sub>CH<sub>2</sub>Si(CH<sub>3</sub>)(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub> (two types)), 0.57 (br s, SiCH<sub>2</sub>CH<sub>2</sub>Si(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>S) (overlapped, 112 H), 1.0 (d, J = 8 Hz, 4.2 H, SiCH(CH<sub>3</sub>)Si), 2.10 (br s, 32 H, SiCH<sub>2</sub>S), 3.05 (br m, 32 H, SCH<sub>2</sub>CH<sub>2</sub>N), 3.27 (br s, 36 H, NCH<sub>3</sub>), 3.67 (br m, 32 H, SCH<sub>2</sub>CH<sub>2</sub>N); <sup>13</sup>C NMR (D<sub>2</sub>O) δ -6.00 (Si(CH<sub>3</sub>)(CH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub> (two types)), -3.72 (Si(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>S), 2.5 (br, Si(CH<sub>2</sub>CH<sub>2</sub>)<sub>4</sub>), 4.28 (SiCH<sub>2</sub>CH<sub>2</sub>SiCH<sub>2</sub>S), 5.00 (br, Si(CH<sub>2</sub>CH<sub>2</sub>Si)<sub>4</sub>), Si(CH<sub>3</sub>)CH<sub>2</sub>CH<sub>2</sub>Si(CH<sub>3</sub>)(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>), 6.77 (SiCH<sub>2</sub>CH<sub>2</sub>SiCH<sub>2</sub>S), 16.23 (SiCH<sub>2</sub>S), 28.01 (SCH<sub>2</sub>CH<sub>2</sub>N), 53.15 (NCH<sub>3</sub>), 65.17 (SCH<sub>2</sub>CH<sub>2</sub>N); <sup>29</sup>Si NMR (D<sub>2</sub>O) δ 3.31 (16 Si, SiCH<sub>2</sub>S), 7.36 (Si(CH<sub>2</sub>CH<sub>2</sub>SiCH<sub>3</sub>)<sub>4</sub>), 7.62 (Si(CH<sub>3</sub>)CH<sub>2</sub>CH<sub>2</sub>SiCH<sub>2</sub>S) (overlapped, 12 Si), 8.78 (1 Si, Si(CH<sub>2</sub>CH<sub>2</sub>)<sub>4</sub>). Anal. Calcd for C<sub>196</sub>H<sub>484</sub>Cl<sub>16</sub>N<sub>16</sub>S<sub>16</sub>Si<sub>29</sub>: Cl, 11.43. Found: total halogen (Calcd as Cl), 10.98.

**Solubilization Studies.** Solutions of **2G-16SO<sub>3</sub>Na** in D<sub>2</sub>O were prepared in 5.00 mL volumetric flasks with concentrations of 9.70 × 10<sup>-3</sup>, 3.88 × 10<sup>-3</sup>, and 1.55 × 10<sup>-3</sup> M. Nine mixtures were made in NMR tubes of the three solutions and the three alkyl-substituted benzene derivatives C<sub>6</sub>H<sub>5</sub>R (R = Me, Et, *n*-Pr); each mixture contained 1 mL of one of the three dendrimer solutions and 0.2 g of one of the three organic compounds. All samples were tightly sealed and sonicated at 50 °C for 16 h. After being removed from the sonicator bath, samples were equilibrated 2 d in an oil bath whose temperature was maintained at 24 ± 1 °C. Samples were removed from the oil bath, cleaned, and quickly transferred to the probe of an NMR spectrometer. Concentrations of solubilized alkylbenzenes were determined from the averages of the ratios of the integrated areas of the alkylbenzene alkyl resonances to the dendrimer amphiphilic group resonances. The results are plotted in Figure 1. After the solubilization experiments, **2G-16SO<sub>3</sub>Na** could be recovered unchanged (as determined by <sup>1</sup>H NMR spectroscopy) by washing the aqueous layer with hexanes and evaporating.

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**Supporting Information Available:** <sup>1</sup>H, <sup>13</sup>C, and <sup>29</sup>Si NMR spectra for all new compounds and MALDI-TOF mass spectra for **OG-4OH**, **1G-8OH**, **2G-16CH<sub>2</sub>Cl**, **2G-16NMe<sub>2</sub>**, and **2G-16SO<sub>3</sub>Na** (65 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.