Thioether Derivatives of Carbosilane Dendrimers of Lower Generations: Synthesis and Complexation with $CuCl_2$

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Summary: Novel carbosilane dendrimers containing thioether groups were synthesized. The possibility of using these compounds as ligands for complexation with transition metal salts, in particular with $CuCl_2$, was investigated. The average maximum numbers of Cu^{2+} ions that can be encapsulated within sulfur containing polymers and dendrimers were estimated.

Keywords: carbosilane dendrimer; hyperbranched; hydrothiolation; metal-polymer complexes; spectrophotometric titration

Introduction

Inorganic nanoparticle/dendrimer nanocomposites received considerable attention in the past decade due to their unique properties (catalytic, optical, magnetic, biomedical, electrical, etc.).[1,2] One of the methods to obtain such nanocomposites is the use of dendrimers as nanocontainers for the stabilization of a single nanoparticle inside the dendrimer molecule. A necessary condition for the creation of such composite materials is the introduction of metal ions into the dendritic structure, which is usually achieved by complexation of the dendrimer with transition metal salts.

Quite a few publications devoted to the study of complex formation of dendrimers with transition metal salts appeared by now. Poly(propylene imine) (PPI)[3,4] and poly(amidoamine) (PAMAM)[5,6] dendrimers are mostly used for that due to their commercial availability, as well as high complexing ability specified by the presence of nitrogen atoms.

A number of articles describes the synthesis of various sulfur-containing dendrimers via hydrothilation reaction.[7–9] Convenience of the reaction and practically absence of side products makes it promising in the synthesis of carbosilane hyperbranched systems and multifunctional compounds.[10–12] The introduction of heteroatoms (sulfur atoms) in the carbosilane dendrimer structure enables the complexation of such dendrimer with transition metal salts and the subsequent creation of a dendrimer-encapsulated particles. Adding large alkyl substituents on the surface of sulfur containing carbosilane dendrimer creates a barrier isolating the dendrimer interior.[13] These compounds may be promising for the stabilization of metal particles inside them.

Studies of complexation of dendrimer molecules with various transition metal salts including copper salts[1] showed that copper salts complexes are not only convenient models for study of complexation processes,[14] but also have practical applications, for example in catalysis[15–18] and environmental protection.[19]

Different methods are used to calculate the amount of transition metal salts complexed with the dendrimers. In particular, spectrophotometric titration,[4,5,20] isomolar series method[21] and mass spectrometry[6] are used in the study of complexation with copper salts.

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The aim of the present work was the synthesis of thioether derivatives of carbosilane dendrimers with sulfur atoms in the inner sphere and estimation of their complexation ability with copper salts.

Results and Discussion

Hydrothiolation reaction was used for the synthesis of thioether derivatives of carbosilane dendrimers of lower generations (Figure 1). This reaction is initiated by UV irradiation and is completed in 30 minutes.

Dendrimer G1-4S-Bu was obtained via two-stage synthesis: hydrothiolation reaction of tetraallylsilane with 3-(mercaptopropylmethyl)dimethoxysilane followed by blocking of the intermediate methoxy-derivative with butyllithium.

Dendrimers G1-8S-Dec and G3-32S-Dec were obtained from polyallylcarbosi-

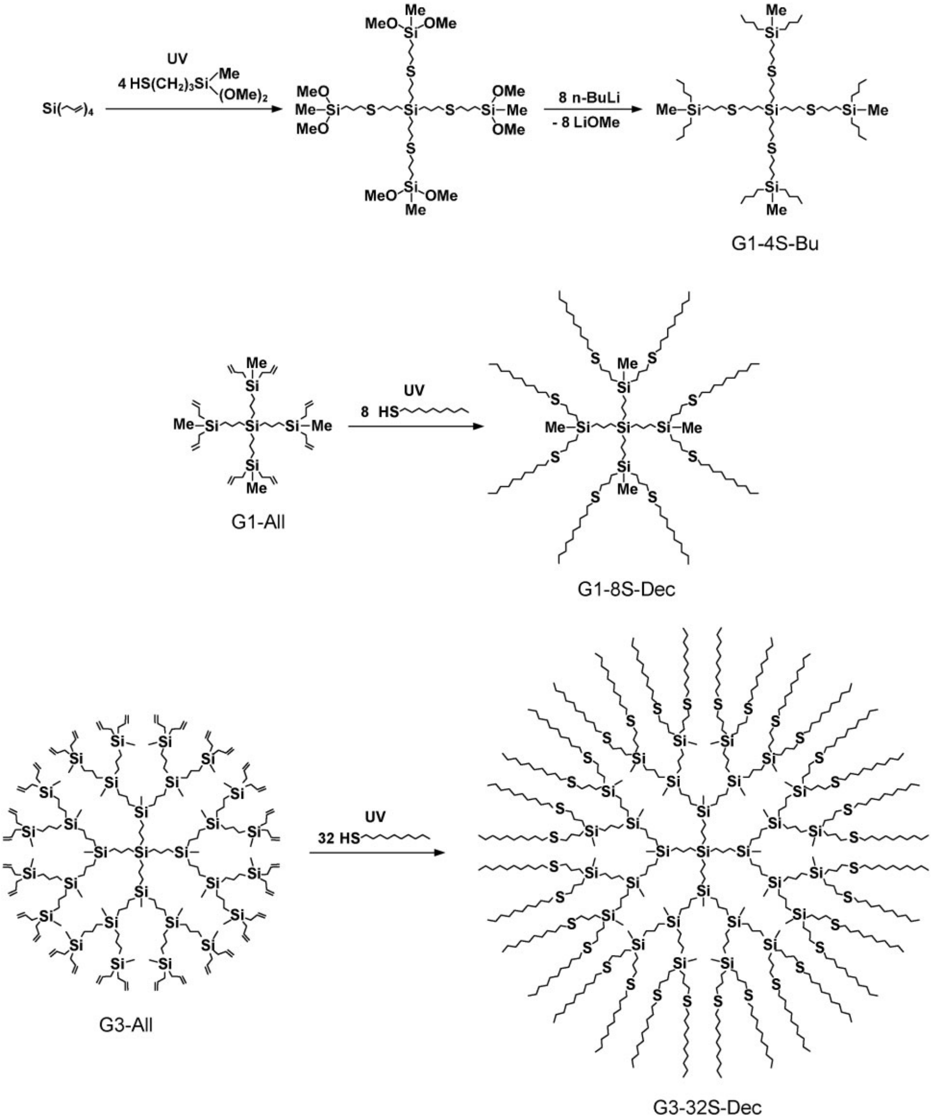

Figure 1.
Scheme of the synthesis of G1-4S-Bu, G1-8S-Dec and G3-32S-Dec.

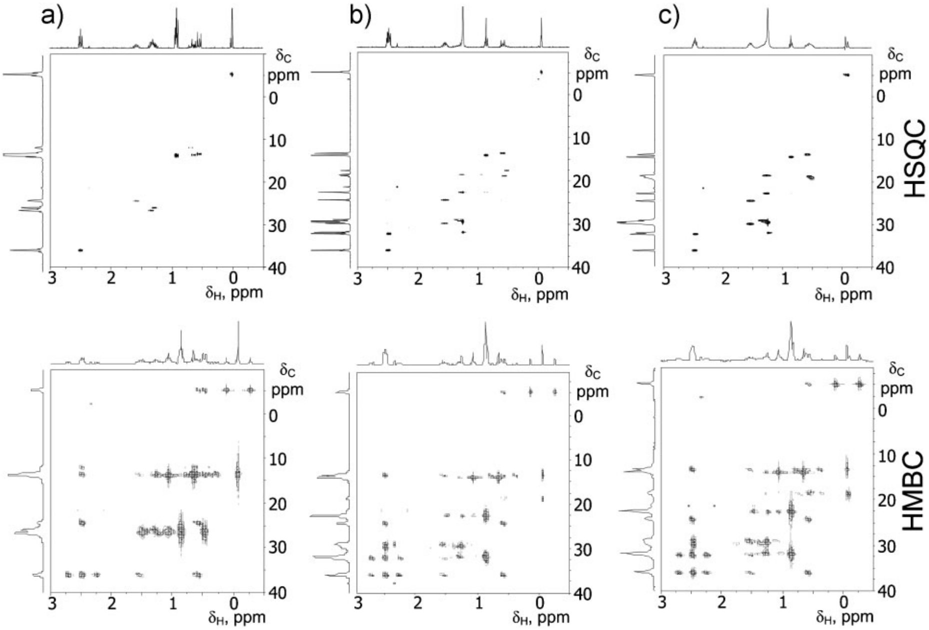

Figure 2.
$^1H/^{13}C$ HSQC/HMBC 2D NMR spectra of G1-4S-Bu (a), G1-8S-Dec (b) and G3-32S-Dec (c).

lane dendrimers of corresponding generations by hydrothiolation reaction with 1-decanethiol. Polyallylcarbosilane dendrimers of 1st and 3d generations were previously synthesized by alternation of the organomagnesium synthesis and hydrosilylation reactions.[22] In all cases benzophenone (1 mol % relative to the reaction mixture) was added as photoinitiator and thiol was taken in 10% excess to the stoichiometry.

Obtained dendrimers were studied by multinuclear $^1H/^{13}C/^{29}Si$ NMR spectroscopy. Identification of signals in ^1H NMR spectra was performed using Total Correlation Spectroscopy (TOCSY) and Correlation Spectroscopy (COSY) methods. The completeness of the reactions was monitored by disappearing of signals at δ 4.82, 5.82 ppm (hydrothiolation) and 3.5 ppm (blocking with butyllithium) in the ^1H NMR spectra. ^1H NMR spectra of compounds are similar with the exception of integral intensities of proton signals of corresponding groups. In particular, all spectra are characterized by presence of resonances at δ 2.49 ppm (for G1-4S-Bu), and at δ 2.47, 2.49 ppm (for decyl derivatives) corresponding to thioether groups. The assignment of signals in $^{13}C/^{29}Si$ NMR spectra was performed using Heteronuclear Single Quantum Coherence (HSQC) and Heteronuclear Multiple-Bond Correlation (HMBC) methods (Figure 2). ^{13}C NMR spectra of G1-8S-Dec and G3-32S-Dec are virtually identical, since these dendrimers are homologues. Chemical shifts of carbon atoms in thioether groups SCH_2 are δ 36.1 ppm (for the $SiCH_2CH_2\mathit{C}H_2S$ fragment) and δ 32.2 ppm (for decyl fragment). In ^{29}Si NMR spectra the sulfur influence shifts the silicon signal to stronger field area, thus chemical shifts are δ 2.52–3.21 ppm for silicon in the $Si(CH_2)_3S$ fragments and δ 0.47–0.9 ppm in $Si(CH_2)_3Si$ fragments.

The target products were purified by preparative chromatography. Figure 3 shows GPC curves of isolated products as monomodal narrow peaks confirming purity of the obtained compounds. Decrease of the elution time upon modification

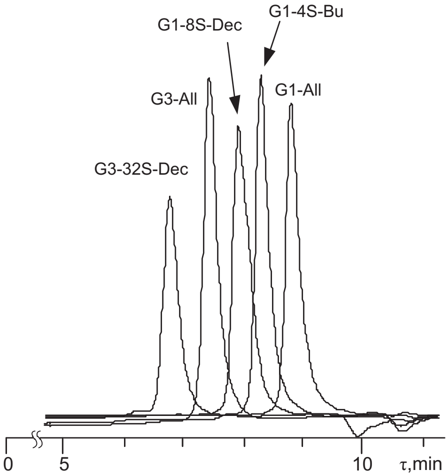

Figure 3.
GPC curves of initial and sulfur containing dendrimers.

indicates increase of hydrodynamic radii of the modified dendrimers.

The composition of obtained dendrimers was confirmed by elemental analysis.

$CuCl_2$ was used to estimate the complexation ability of thioether derivatives of carbosilane dendrimers and previously synthesized hyperbranched polymers HB-S-Dec and HB-S-Bu,[23] which are convenient and more affordable models for the study of properties of carbosilane dendritic systems.[24] Mixture of $CHCl_3$ and MeOH (4:1, v/v) was used as a solvent in the study of complexation processes.

Qualitative assessment of the formation of copper salts/polymer complexes was performed using a UV-visible spectroscopy. In the absence of Cu^{2+} ion sulfur containing polymer or dendrimer does not absorb light in the range of 300–1000 nm, whereas $CuCl_2$ alone in the mixed solvent reveals a broad absorption peak centered around 900 nm and rather narrow band at 300 nm. Upon adding copper salt to the polymer or dendrimer solution new absorption band with maximum at 450 nm appears. Figure 4 shows UV-visible absorption spectra of hyperbranched polymer HB-S-Dec, $CuCl_2$ and their mixture (for thioether derivatives of carbosilane dendrimers spectra are similar).

Quantitative estimation of the stoichiometry of complex formation was performed by means of spectrophotometric titration. This method enables one to assess the average maximum number of Cu^{2+} ions that can be encapsulated within sulfur containing polymer.

Measurements were carried out at 450 nm absorption band. Figure 5 shows the absorption spectra of the solutions

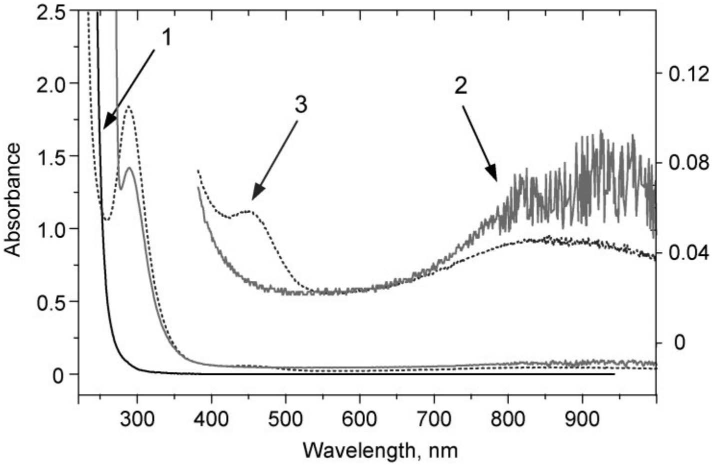

Figure 4.
Absorbance spectra of HB-S-Dec solution (1), $CuCl_2$ solution in the absence (2) and in the presence (3) of HB-S-Dec.

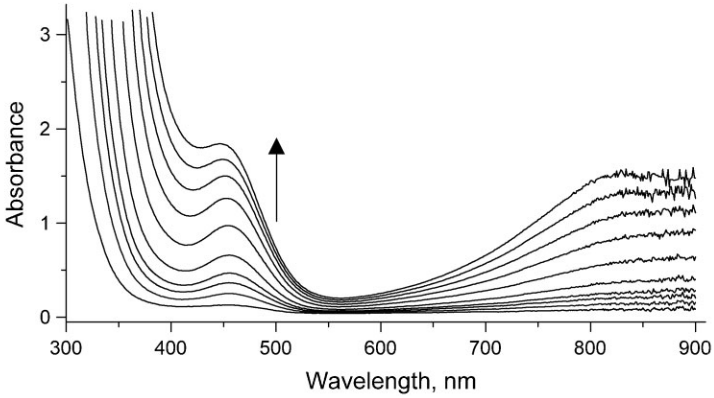

Figure 5.
Experimental absorbance spectra for $CuCl_2$ complexes with HB-S-Dec. The concentration of HB-S-Dec is 10^{-2} $(mol \cdot L^{-1})$, while molar ratio of metal ion to ligand increases from 0 to 5.

containing the same amounts of hyperbranched polymer HB-S-Dec and different amounts of $CuCl_2$.

Spectrophotometric titration curves based on obtained data are shown in Figure 6. Figure 6a shows the absorbance versus the number of copper ions per repeating unit of hyperbranched polymer HB-S-Dec, while Figure 6b–d shows the absorbance versus the number of copper ions per molecule of dendrimers G1-4S-Bu, G1-8S-Dec, G3-32S-Dec (the number of sulfur atoms is 4, 8 and 32, respectively). The curves have two distinct linear regions. The number of Cu^{2+} ions, corresponding to the intersection point of the lines extra-

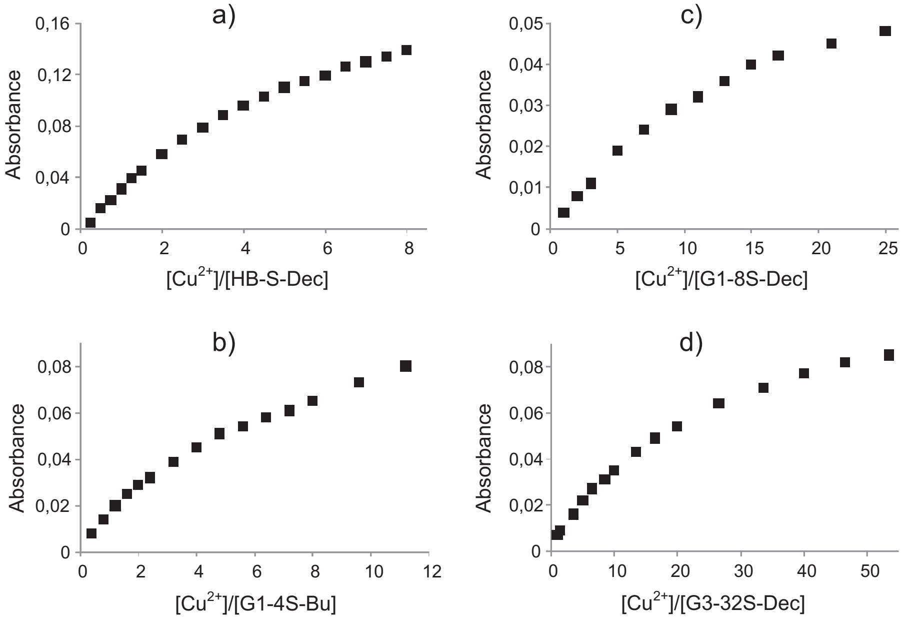

Figure 6.
Spectrophotometric titration curves recorded at $\lambda = 450$ nm for different ratios of $[Cu^{2+}]/[X]$ for (a) X = repeating unit of HB-S-Dec, (b) X = G1-4S-Bu, (c) X = G1-8S-Dec and (d) X = G3-32S-Dec.

Table 1.
The $[Cu^{2+}]/[S]$ stoichiometric ratios, obtained from the spectrophotometric titration curves.

Polymer	HB-S-Dec	HB-S-Bu	G1-8S-Dec	G1-4S-Bu	G3-32S-Dec
$[Cu^{2+}]/[S]$	2:1*	2:1*	1:1	1:2	1:2.5

*molar ratio of Cu^{2+} to the number of sulfur atoms in the repeating unit of hyperbranched polymer.

polating these two regions is regarded as an estimate of the maximum number of Cu^{2+} ions complexed within the polymer.

As follows from Figure 6a the concentration of Cu^{2+} associated with hyperbranched polymer is rather high and stoichiometric ratio $[Cu^{2+}]$/[HB-S-Dec] is 2:1. A similar case was described on the example of complexation of hexanoyl or palmitoyl-modified PPI dendrimers with $CuCl_2$. This was presumably explained by different solubility of the metal ion in dendrimer versus in the solvent.[4] Titration curve of HB-S-Bu coincides with the curve shown in Figure 6a, when the initial concentrations of hyperbranched polymers are the same. In our case hyperbranched polymers are able to encapsulate large amounts of $CuCl_2$ possibly due to the wide molecular weight distribution,[23] the loose structure and an irregular arrangement of sulfur atoms. According to GPC data the polydispersity coefficient (D) of HB-S-Dec is 3.2 (PSS).

Ratios $[Cu^{2+}]$/[Dendrimer] estimated from the titration curves of the dendrimers (Figure 6b–d) are 8:1 for G1-8S-Dec, 2:1 for G1-4S-Bu and about 13:1 for G3-32S-Dec.

Table 1 shows the converted stoichiometric ratios of copper ions to the number of sulfur atoms containing in the polymer molecule. Depending on the structure of the polymer, this ratio varies from 2:1 to 1:2.5.

Conclusion

Thioether derivatives of carbosilane dendrimers of low generations were synthesized by means of hydrothiolation reaction. A comparison of complexation of hyperbranched polymers and dendrimers with copper salts was carried out and showed that complexation efficiency varies in quite wide interval depending on molecular structure specificity of investigated compounds. Adjustment of the latter could be used as an instrument for control of the loading efficiency and complexes stability.

Experimental Part

Ultraviolet radiation was provided by «Camelion LH26-3U» (26W) energy saving UV-lamp with maximum emission at 365 nm.

Multinuclear $^1H/^{13}C/^{29}Si$ NMR spectra were obtained on the «Bruker Avance II 300» spectrometer (300.17/75.48/59.64 MHz). The samples were dissolved in deuterated chloroform $CDCl_3$. Internal standard was tetramethylsilane $SiMe_4$.

GPC analysis was carried out on the «Laboratorni pristroje» liquid chromatograph (Czechoslovakia) equipped with the RIDK-102 refractometer as a detector. Phenogel 75 kD was used as sorbent and the THF was used as eluent.

The preparative chromatographic system consisted of an Akvilon isocratic high pressure pump, an RIDK-102 refractometer as a detector, a 300 mm × 20.2 mm preparative column with Phenogel 10 × 3 Å (10 μm) as a sorbent, and THF as an eluent. The solvents were removed in vacuum (1 Torr) upon heating to 50 °C.

The absorption spectra were recorded on the «Shimadzu-UV2501PC» (Japan) spectrometer. There were used a quarts cuvette with 1 cm optical path.

All the solvents used in this work were dried according to standard techniques.[25] 1-Decanethiol and (3-mercaptopropyl)-methyldimethoxysilane («Aldrich Chemical Co.») were used as received. Benzophenone were recrystallized from methanol before using. There was used anhydrous $CuCl_2$ in spectrophotometric titration.

Procedure of Spectrophotometric Titration

Titration was carried out in the mixture of solvents $CHCl_3$/MeOH (4:1, v/v). Aliquot of $CuCl_2$ solution was added to the cuvette containing 4 mL of polymer solution (optical path 1 cm), equipped with stir bar and cap, using a micropipette. After addition of $CuCl_2$ solution, the cap was placed on the cuvette to prevent solvent evaporation, resulting mixture was stirred for several seconds and then absorbance spectra was recorded.

Following concentrations of solutions were used for titration: 1 mM solutions of HB-S-Dec and HB-S-Bu was titrated with 20 mM solution of $CuCl_2$; 0.5 mM solution of G1-4S-Bu – 16 mM solution of $CuCl_2$; 0.1 mM solution of G1-8S-Dec – 8 mM solution of $CuCl_2$; 0.05 mM solution of G3-32S-Dec – 6.7 mM solution of $CuCl_2$.

Hyperbranched polymers HB-S-Dec and HB-S-Bu were synthesized as described before.[23]

Dendrimer G1-4S-Bu

All operations were carried out under argon atmosphere. Mixture of tetraallylsilane (1.00 g, 0.0052 mol), 3-(mercaptopropylmethil)dimethoxysilane (4.13 g, 0.0229 mol), benzophenone (0.0512 g, 0.281 mmol) in THF (25 ml) was irradiated by UV lamp for 30 minutes under stirring at ambient temperature. After that irradiated mixture was added dropwise to the 16 ml of 1.6 M solution of n- butyllithium in hexane at 0 °C. Resulting mixture was stirred for 20 min at 0 °C and then for 4 h at ambient temperature. Methanol (2 ml) was added dropwise to reaction mixture for the neutralization of n- butyllithium excess. Mixture was washed with water until the neutral reaction, dried with Na_2SO_4, filtered and evaporated under 1 Torr till the constant weight. The product, pale yellow oil (5.08 g, yield 87%), was further purified by preparative chromatography to get target compound. ^{1}H NMR ($CDCl_3$, δ, ppm, *J*/Hz): −0.08 (s, 12H, $\mathrm{SiC}H_3$); 0.48 (m, 16H, $\mathrm{Si(Me)C}H_2$); 0.60 (m, 16H, $\mathrm{SiC}H_2$); 0.87 (t, 24H, $\mathrm{C}H_3$, $J = 6.8$); 1.28 (m, 32H, $\mathrm{C}H_2$); 1.54 (m, 16H, $\mathrm{SCH_2C}H_2$), 2.49 (t, 16H, $\mathrm{C}H_2\mathrm{SC}H_2$, $J = 7.6$). ^{13}C NMR ($CDCl_3$, δ, ppm): -5.2 ($\mathrm{Si}C\mathrm{H_3}$); 12.0 ($\mathrm{Si}C\mathrm{H_2CH_2CH_2S}$); 13.5 ($\mathrm{Si(Me)}C\mathrm{H_2CH_2CH_2CH_3}$); 13.7 ($\mathrm{SCH_2CH_2}C\mathrm{H_2Si(Me)}$) 13.8 ($C\mathrm{H_3}$); 24.4 ($C\mathrm{H_2CH_2S}$); 24.5 ($\mathrm{SCH_2}C\mathrm{H_2}$); 26.1 ($\mathrm{Si(Me)CH_2CH_2}C\mathrm{H_2CH_3}$); 26.7 ($\mathrm{Si(Me)CH_2}C\mathrm{H_2CH_2CH_3}$); 36.1 ($C\mathrm{H_2S}C\mathrm{H_2}$). ^{29}Si NMR ($CDCl_3$, δ, ppm): 3.07 ($Si\mathrm{CH_2CH_2CH_2S}$); 3.21 ($Si\mathrm{Me}$). Found (%): C, 64.45; H, 11.94; S, 11.66; Si, 12.30. $C_{60}H_{132}S_4Si_5$. Calculated (%): C, 64.21; H, 11.(85; S, 11.43; Si, 12.51.

Dendrimer G1-8S-Dec

Mixture of G1-All (1.51 g, 0.0022 mol), 1-decanethiol (3.38 g, 0.0194 mol), benzophenone (0.0394 g, 0.216 mmol) in THF (23 ml) was irradiated by UV lamp for 1 h under stirring at ambient temperature. THF (30 ml) was added to the solution and the resulting mixture was precipitated with EtOH (95 ml). Obtained product was dried in vacuo (1 Torr) till the constant weight to afford a pale-yellow oil (3.62 g, 79%). ^{1}H NMR ($CDCl_3$, δ, ppm, *J*/Hz): -0.05 (s, 12H, $\mathrm{SiC}H_3$); 0.46-0.66 (m, 32H, $\mathrm{SiC}H_2$); 0.87 (t, 24H, $\mathrm{C}H_3$, $J = 6.7$); 1.25 (m, 120H, $\mathrm{C}H_2$); 1.54 (m, 32H, $\mathrm{SCH_2C}H_2$), 2.47 (t, 16H, $\mathrm{SC}H_2$, $J = 7.3$); 2.49 (t, 16H, $\mathrm{C}H_2\mathrm{S}$, $J = 7.4$). ^{13}C NMR ($CDCl_3$, δ, ppm): -5.2 ($\mathrm{Si}C\mathrm{H_3}$); 13.5 ($\mathrm{Si(Me)}C\mathrm{H_2CH_2CH_2S}$); 14.1($C\mathrm{H_3}$); 17.6 ($\mathrm{Si}C\mathrm{H_2}$); 18.5 ($\mathrm{SiCH_2}C\mathrm{H_2CH_2Si}$); 18.8 ($\mathrm{SiCH_2CH_2}C\mathrm{H_2Si(Me)}$); 22.6 ($C\mathrm{H_2CH_3}$); 24.4 ($\mathrm{SiCH_2}C\mathrm{H_2CH_2S}$); 29.0 ($\mathrm{S(CH_2)_2}C\mathrm{H_2}$); 29.3 ($\mathrm{S(CH_2)_2}C\mathrm{H_2(CH_2)_3}C\mathrm{H_2}$); 29.6 ($\mathrm{S(CH_2)_4}C\mathrm{H_2}C\mathrm{H_2}$); 29.8 ($\mathrm{SCH_2}C\mathrm{H_2}$); 31.9 ($C\mathrm{H_2CH_2CH_3}$); 32.2 ($\mathrm{S}C\mathrm{H_2}$); 36.1 ($C\mathrm{H_2S}$). ^{29}Si NMR ($CDCl_3$, δ, ppm): 0.47 ($Si\mathrm{CH_2CH_2CH_2Si}$); 2.52 ($Si\mathrm{Me}$). Found (%): C, 68.99; H, 12.12; S, 12.11; Si, 6.84. $C_{120}H_{252}S_8Si_5$. Calculated (%): C, 68.89; H, 12.14; S, 12.26; Si, 6.71.

Dendrimer G3-32S-Dec was synthesized in similar way as G1-8S-Dec from the mixture of G3-All (1.11 g, 0.298 mmol), 1-decanethiol (1.83 g, 0.0105 mol), benzophenone (0.0197 g, 0.108 mmol) in THF (14 ml). Irradiation time was 3 h. Product was obtained as a pale yellow oil (2.72 g, 98%). The target product was isolated by preparative chromatography. ^{1}H NMR ($\mathrm{CDCl_3}$, δ, ppm, *J*/Hz): −0.09, −0.05 (s, 84H, $\mathrm{SiC}\mathit{H}_3$); 0.55 (m, 176H, $\mathrm{SiC}\mathit{H}_2$); 0.87 (t, 96H, $\mathrm{C}\mathit{H}_3$, $J = 6.3$); 1.25 (m, 504H, $\mathrm{C}\mathit{H}_2$); 1.56 (m, 128H, $\mathrm{SCH_2C}\mathit{H}_2$), 2.47 (t, 64H, $\mathrm{SC}\mathit{H}_2$, $J = 7.5$); 2.49 (t, 64H, $\mathrm{C}\mathit{H}_2\mathrm{S}$, $J = 7.4$). ^{13}C NMR ($\mathrm{CDCl_3}$, δ, ppm): -5.0, -5.1 ($\mathrm{Si}\mathit{C}\mathrm{H_3}$); 13.5 ($\mathrm{Si(Me)}\mathit{C}\mathrm{H_2CH_2CH_2S}$); 14.1($\mathit{C}\mathrm{H_3}$); 17.8 ($\mathrm{Si}\mathit{C}\mathrm{H_2}$); 18.5 ($\mathrm{SiCH_2}\mathit{C}\mathrm{H_2CH_2Si}$); 18.9 ($\mathrm{Si(Me)}\mathit{C}\mathrm{H_2}$); 22.7 ($\mathit{C}\mathrm{H_2CH_3}$); 24.3 ($\mathrm{SiCH_2}$-$\mathit{C}\mathrm{H_2CH_2S}$); 28.9 ($\mathrm{S(CH_2)_2}\mathit{C}\mathrm{H_2}$); 29.4 ($\mathrm{S(CH_2)_2}\mathit{C}\mathrm{H_2(CH_2)_3}\mathit{C}\mathrm{H_2}$); 29.6 ($\mathrm{S(CH_2)_4}$-$\mathit{C}\mathrm{H_2}\mathit{C}\mathrm{H_2}$); 29.7 ($\mathrm{SCH_2}\mathit{C}\mathrm{H_2}$); 31.9 ($\mathit{C}\mathrm{H_2CH_2}$-$\mathrm{CH_3}$); 32.2 ($\mathrm{S}\mathit{C}\mathrm{H_2}$); 36.1 ($\mathit{C}\mathrm{H_2S}$). ^{29}Si NMR ($\mathrm{CDCl_3}$, δ, ppm): 0.78 ($\mathit{Si}\mathrm{CH_2CH_2CH_2Si}$); 0.90 ($\mathit{Si}\mathrm{(Me)CH_2CH_2CH_2Si}$); 2.53 ($\mathit{Si}\mathrm{(Me)}$-$\mathrm{CH_2CH_2CH_2S}$). Found (%): C, 67.92; H, 12.04; S, 10.91; Si, 8.95. $\mathrm{C_{528}H_{1116}S_{32}Si_{29}}$. Calculated (%): C, 68.14; H, 12.09; S, 11.02; Si, 8.75.

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