

# Preparation and Unequivocal Identification of Chromophores-Substituted Carbosilane Dendrimers up to 7<sup>th</sup> Generations

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*Received January 8, 2009, Accepted March 3, 2009*

Bis(phenylethynyl)dimethylsilane is branched by the hydrosilation of the phenylethynyl group with dichloromethylsilane, and then the resulting chlorosilane is reacted with lithium phenylacetylide to give the 1<sup>st</sup> generation. The same hydrosilation and alkynylation are repeated to obtain the 7<sup>th</sup> generation. In addition peripheral Si-Cl moiety of the seven kind generation dendrimers are reacted with alcoholic moiety of 9-hydroxymethylanthracene and 2-(2-hydroxyphenyl)benzoxazole group in the presence of TMEDA. Then three kinds of carbosilane dendrimers are prepared from the 1<sup>st</sup> to the 7<sup>th</sup> generations, the 7<sup>th</sup> generation of each dendrimer has 256 phenylethynyl, 256 9-anthracenylmethoxy, or 128 2-(2-phenoxy)benzoxazole groups. Each synthesized dendrimer is unequivocally characterized by <sup>1</sup>H and <sup>13</sup>C NMR, elemental analysis, MALDI-MS, GPC, and PL (photoluminescence). Characteristically PDI (Polydisperse Index) values of the dendrimers' peak in GPC are in the range of 1.00~1.07, which indicates that each generation of carbosilane is in unified distribution. PL spectra of phenylethynyl and 9-anthracenylmethoxy group substituted dendrimers show no significant change with increasing the generation from the 1<sup>st</sup> to the 7<sup>th</sup>. However, the PL spectra of 2-(2-phenoxy)benzoxazole group substituted dendrimers show a blue-shift trend with increasing the generation from the 1<sup>st</sup> to the 7<sup>th</sup>.

**Key Words:** Dendrimer, Silane, Siloxane, Photoluminescence, GPC

## Introduction

Since Vögtle reported the first cascade synthesis<sup>1,2</sup> new homologous dendritic molecules have been prepared.<sup>3-5</sup> Nowadays the application of dendrimer becomes more important issue for many researchers.<sup>6-13</sup> Defect free dendritic structures (dendrons or dendritic wedges are structurally monomolecular or unimolecular in composition) are available by the using the limited number of reactions under controlled reaction conditions of temperature, pressure, and large excess of reagents.<sup>14-17</sup> In the case of general polymer it is well known that every chain reaction provides a mixture of molecular linear polymers.

It has been a controversial subject to confirm the molecularity of dendrimer (molecular purity or structural defect), especially that of higher generation dendrimer due to the self-similarity inherent in the dendritic architecture.<sup>15,18</sup> For lower generation dendrimer, the molecular weight of which is around thousands Daltons, the unimolecularity has been confirmed by mass spectroscopy.<sup>18-19</sup> MS (Mass Spectroscopy) is useful to determine the molecular weight of lower generation dendrimer with its molecular ion peak and fragmentation pattern, but it still gives no decisive information for its structural defect of higher generations.<sup>20</sup> In this reason GPC (The gel permeation chromatography) is used to determine the unimolecularity of dendrimer.<sup>16,21</sup>

Herein, novel carbosilane dendrimers (1<sup>st</sup> to 7<sup>th</sup> generation), having chromophores of phenylethynyl, anthracenyl, and benzoxazolyl groups on the periphery, are synthesized and characterized by <sup>1</sup>H and <sup>13</sup>C NMR, MALDI-MS, and elemental analysis. their unimolecularities are confirmed by GPC. Additionally dendritic effects of the chromophores of

them are studied by PL (photoluminescence). The purpose of the article is observation of unimolecularities of these carbosilane dendrimers and dendritic effect of them is studied by PL (photoluminescence) spectroscopy.

## Experimental

All reactions were carried out under a dried nitrogen atmosphere attached to vacuum line. NMR spectra were recorded on a Bruker AC 200. UV spectra were measured by HP 8452A diode array ultraviolet visible spectrophotometer. The GPC was performed in THF at 25 °C with Waters 515 HPLC pump and Waters 2410 Refractive Index Detector connected with 3 columns (Ultrastayragel 0.78 x 30 cm; 10<sup>3</sup>, 10<sup>4</sup> and 10<sup>5</sup>), which was calibrated by narrow molecular weight of polystyrene standard. Elemental analyses were carried out at KBSI in Daegu, Korea. The following abbreviations are used: PA refers to phenyl ethylenyl, AN refers to anthracene, BO refers to benzoxazolyl group, TMEDA refers to tetramethylethylenediamine. In the representation of nG[2,2<sup>n-1</sup>.1]-2<sup>n</sup>X and nG[2,2<sup>n-1</sup>.2]-2<sup>n+1</sup>X; the n<sup>th</sup>G refers to generation number, the first 2 in bracket refers to the number of branch in core, the 2<sup>n-1</sup> refers to the number of branches in inside and last 1 or 2 in the bracket refers to the number of functional groups on the periphery and last 2<sup>n</sup>X or 2<sup>n+1</sup>X refers to the number of X functional groups on the whole periphery. Hydrosilation of triple bonds on dendritic periphery and alkylation by lithium phenylacetylide were described in the previous reports.<sup>15</sup>

Dichloromethylsilane is used for the hydrosilation of the preparation of nG[2,2<sup>n-1</sup>.2]-2<sup>n-1</sup>PA and nG[2,2<sup>n-1</sup>.2]-2<sup>n-1</sup>AN,

chlorodimethylsilane is used for the hydrosilation of the preparation of nG[2.2<sup>n-1</sup>,1]-2<sup>n</sup>BO.

**(1) Synthesis of nG[2.2<sup>n-1</sup>,2]-2<sup>n+1</sup>PA type dendrimers.**

**1G[2,0,2]-4PA:** 55 mL (55 mmol) of lithium phenylacetylide (1 M in THF) was added to the solution of 5.65 g (11.52 mmol) of 1G[2,0,2]-4Cl in 50 mL of THF at room temperature. Then, the reaction mixture was refluxed for 2 hrs. After removing solvent from the mixture, toluene was added to the residue. Lithium chloride salt was removed by filtration with continual adding of activated charcoal until to remove the brown color. 1G[2,0,2]-4PA was purified by silica gel chromatography with mixed solvent of toluene and hexane (1:1). Yield: 7.79 g (89%, 11.52 mmol) as light yellow to white powder. <sup>1</sup>H-NMR (ppm, CDCl<sub>3</sub>): δ -0.38 (s, 6H, SiMe, G0), 0.40 (s, 6H, SiMe, G1), 6.71 (s, 2H, CH=C), 7.12~7.45 (m, 30H, Ph, G0~G1). <sup>13</sup>C-NMR (ppm, CDCl<sub>3</sub>): δ -0.98 (SiMe, G0), -0.67 (SiMe, G1), 148.52, 157.96 (C=C), 89.22, 107.61 (C≡C), 122.70, 122.77, 132.12 (Ph, G1), 126.41, 128.21, 128.89, 143.21 (Ph, G0). Anal. Calc. for C<sub>52</sub>H<sub>44</sub>Si<sub>3</sub> (753.2): C, 82.86%, H, 5.84%. Found: C, 82.82%, H, 5.82%. MALDI-TOF mass: 775.31 (M+Na)<sup>+</sup>. UV/Vis, λ<sub>max</sub> 253 nm, ε<sub>max</sub> 0.64 × 10<sup>5</sup>. GPC: PDI value (M<sub>w</sub>/M<sub>n</sub>), 1.01 (753/739); Retention time (Rt), 19.66 min.

**2G[2,2,2]-8PA:** 4.54 g (3.74 mmol) of 2G[2,2,2]-8Cl and 40 mL (40 mmol) of lithium phenylacetylide were used by the same procedure as the above for 1G[2,0,2]-4PA. The mixture was refluxed for 5 hrs. Yield: 5.74 g (89%, 3.30 mmol) as yellow glassy material. <sup>1</sup>H-NMR (ppm, CDCl<sub>3</sub>): δ -0.70 (s, 6H, SiMe, G0), -0.51 (s, 6H, SiMe, G1), 0.39 (s, 12H, SiMe, G2), 6.10 (s, 2H, CH=C, G0), 6.71 (s, 4H, CH=C, G1), 6.90~7.47 (m, 70H, Ph, G0~G2). <sup>13</sup>C-NMR (ppm, CDCl<sub>3</sub>): δ -3.06 (SiMe, G0), -0.53 (SiMe, G1), -0.95 (SiMe, G2), 144.91, 162.68 (C=C, G0), 145.89, 158.40 (C=C, G1), 89.24, 107.52 (C≡C), 125.90, 127.59, 128.12, 128.19, 128.84 (Ph, G0~G1), 126.43, 122.71, 127.72, 132.10 (Ph, G2). Anal. Calc. for C<sub>120</sub>H<sub>100</sub>Si<sub>7</sub> (1738.7): C, 82.82%, H, 5.75%. Found: C, 82.40%, H, 5.84%. MALDI-TOF mass: 1761.83 (M+Na)<sup>+</sup>. UV/Vis, λ<sub>max</sub> 253 nm, ε<sub>max</sub> 1.12 × 10<sup>5</sup>. GPC: PDI value (M<sub>w</sub>/M<sub>n</sub>), 1.01 (1209/1188); Rt, 18.76 min.

**3G[2,2,2,2]-16PA:** 4.79 g (1.87 mmol) of 3G[2,2,2,2]-16Cl and 40 mL (40 mmol) of lithium phenylacetylide were used by the same procedure as the above for 1G[2,0,2]-4PA. The mixture refluxed for 10 hrs. Yield: 5.27 g (76%, 1.42 mmol) as yellow glassy material. <sup>1</sup>H-NMR (ppm, CDCl<sub>3</sub>): δ -0.76 (s, 6H, SiMe, G0), -0.61 (s, 6H, SiMe, G1), -0.80 (s, 12H, SiMe, G2), 0.34 (s, 24H, SiMe, G3), 5.93 (s, 2H, CH=C, G0), 6.03 (s, 4H, CH=C, G1), 6.56 (s, 4H, C=C, G2), 6.57~7.43 (m, 150H, Ph, G0~G3). <sup>13</sup>C-NMR (ppm, CDCl<sub>3</sub>): δ -2.42 (SiMe, G0), -0.16 (SiMe, G1), -3.29 (SiMe, G2), -0.92 (SiMe, G3), 142.90, 144.58 (C=C, G0), 143.04, 163.65 (C=C, G1), 145.40, 158.31 (C=C, G2), 89.25, 107.48 (C≡C), 127.59, 122.71, 128.45, 132.08 (Ph, G3), 125.29, 125.99, 126.40, 127.71, 128.08, 128.18, 129.04, 129.18, 158.83 (Ph, G0~G2). Anal. Calc. for C<sub>256</sub>H<sub>212</sub>Si<sub>15</sub> (3709.7): C, 82.80%, H, 5.71%. Found: C, 82.43%, H, 5.92%. MALDI-TOF mass: 3723 (M+Na)<sup>+</sup>. UV/Vis, λ<sub>max</sub> 253 nm, ε<sub>max</sub> 2.12 × 10<sup>5</sup>. GPC: PDI value (M<sub>w</sub>/M<sub>n</sub>), 1.03 (3166/3069); Rt, 17.25 min.

**4G[2,2,2,2,2]-32PA:** 3.00 g (0.54 mmol) of 4G[2,2,2,2,2]-

32Cl and 20 mL (20 mmol) of lithium phenylacetylide were used by the same procedure as the above for 1G[2,0,2]-4PA. The mixture refluxed for 10 hrs. Yields: 3.13 g (76%, 0.41 mmol) as yellow glassy material. <sup>1</sup>H-NMR (ppm, CDCl<sub>3</sub>): δ -0.88, -0.84, -0.83 (s, 48H, SiMe, G0~G3), 0.31 (s, 48H, SiMe, G4), 5.80~6.98, 6.46~6.60 (30H, CH=C, G0~G3), 6.60~6.76, 6.76~7.62 (m, 310H, Ph, G0~G4). <sup>13</sup>C-NMR (ppm, CDCl<sub>3</sub>): δ -3.26 (SiMe, G0~G2), -1.10 (SiMe, G3), -0.80 (SiMe, G4), 89.16, 107.48 (C≡C), 142.82, 144.49, 145.34, 158.13 (C=C, G0~G3), 122.58, 126.30, 127.64, 128.04, 128.95, 131.80, 132.19, 163.65 (Ph, G0~G2). Anal. Calc. for C<sub>528</sub>H<sub>436</sub>Si<sub>31</sub> (7,640): C, 82.93%, H, 5.70%. Found: C, 81.99%, H, 5.79%. MALDI-TOF mass: 7674.63 (M+Na)<sup>+</sup>. UV/Vis, λ<sub>max</sub> 253 nm, ε<sub>max</sub> 4.47 × 10<sup>5</sup>. GPC: PDI (M<sub>w</sub>/M<sub>n</sub>), 1.04 (5,292/5,075); Rt, 16.35 min.

**5G[2,2,2,2,2,2]-64PA:** 3.0 g (0.26 mmol) of 5G[2,2,2,2,2]-64Cl and 20 mL (20 mmol) of lithium phenylacetylide were used by the same procedure as the above for 1G[2,0,2]-4PA. The mixture refluxed for 10 hrs. Yield: 3.22 g (79%, 0.20 mmol) as yellow glassy material. <sup>1</sup>H-NMR (ppm, CDCl<sub>3</sub>): δ -1.06 ~ -0.64 (96H, SiMe, G0~G4), 0.16~0.48 (96H, SiMe, G5), 5.78~6.02, 6.48~6.58 (62H, CH=C, G0~G5), 6.48~6.76, 6.76~7.64 (630H, Ph, G0~G5). <sup>13</sup>C-NMR (ppm, CDCl<sub>3</sub>): δ -3.21 (SiMe, G0~G4), -0.90 (SiMe, G5), 89.30, 107.51 (C≡C), 142.85, 144.52, 145.34, 158.13 (C=C, G0~G4), 122.65, 126.39, 127.60, 128.21, 128.85, 132.05, 132.19, 164.23 (Ph, G0~G2). Anal. Calc. for C<sub>1072</sub>H<sub>884</sub>Si<sub>63</sub> (15,512): C, 82.93%, H, 5.70%. Found: C, 82.65%, H, 5.43%. UV/Vis, λ<sub>max</sub> 253 nm, ε<sub>max</sub> 8.16 × 10<sup>5</sup>. GPC: PDI (M<sub>w</sub>/M<sub>n</sub>), 1.04 (11,226/10,709); Rt, 16.02 min.

**6G[2,2,2,2,2,2,2]-128PA:** 3.0 g (0.13 mmol) of 6G[2,2,2,2,2,2,2]-128Cl and 20 mL (20 mmol) of lithium phenylacetylide were used by the same procedure as the above for 1G[2,0,2]-4PA. The mixture refluxed for 10 hrs. Yield: 3.00 g (74%, 0.095 mmol) as yellow glassy material. <sup>1</sup>H-NMR (ppm, CDCl<sub>3</sub>): δ -0.96 ~ -0.60 (192H, SiMe, G0~G5), 0.20~0.49 (192H, SiMe, G6), 5.82~6.14 (126H, CH=C, G0~G5), 6.50~7.68 (1270H, Ph, G0~G6). <sup>13</sup>C-NMR (ppm, CDCl<sub>3</sub>): δ -3.12 (SiMe, G0~G5), -0.90 (SiMe, G6), 89.34, 107.50 (C≡C), 142.83, 144.49, 144.81, 145.40, 158.00 (C=C, G0~G5), 122.63, 126.49, 127.60, 128.05, 128.20, 128.83, 132.03, 163.38 (Ph, G0~G6). Anal. Calc. for C<sub>2160</sub>H<sub>1780</sub>Si<sub>127</sub> (31,256): C, 82.93%, H, 5.69%. Found: C, 82.26%, H, 5.69%. UV/Vis, λ<sub>max</sub> 253 nm, ε<sub>max</sub> 1.36 × 10<sup>6</sup>. GPC: PDI (M<sub>w</sub>/M<sub>n</sub>), 1.07 (14,747/13,774); Rt, 15.54 min.

**7G[2,2,2,2,2,2,2,2]-256PA:** 1.00 g (0.022 mmol) of 7G[2,2,2,2,2,2,2,2]-256Cl and 7 mL (7 mmol) of lithium phenylacetylide were used by the same procedure as the above for 1G[2,0,2]-4PA. The mixture refluxed for 10 hrs. Yield: 1.08 g (82%, 0.017 mmol) as yellow glassy material. <sup>1</sup>H-NMR (ppm, CDCl<sub>3</sub>): δ -1.05 ~ -0.70 (384H, SiMe, G0~G6), 0.02~0.50 (384H, SiMe, G7), 5.78~6.02 (254H, CH=C, G0~G6), 6.29~7.60 (m, 2550H, Ph, G0~G5). <sup>13</sup>C-NMR (ppm, CDCl<sub>3</sub>): δ -4.60 ~ -2.00 (SiMe, G0~G5), -0.88 (SiMe, G7), 89.43, 107.50 (C≡C), 142.79, 144.50, 145.34, 158.26 (C=C, G0~G6), 122.64, 126.39, 128.21, 129.03, 132.02, 163.43 (Ph, G0~G7). Anal. Calc. for C<sub>4336</sub>H<sub>3572</sub>Si<sub>255</sub> (62,744): C, 82.93%, H, 5.69%. Found: C, 82.04%, H, 5.82%. UV/Vis, λ<sub>max</sub> 253 nm, ε<sub>max</sub> 2.32

$\times 10^6$ . GPC: PDI value ( $M_w/M_n$ ), 1.05 (17,109/16,165); Rt, 15.15 min.

**(2) Preparation and characterization of the dendrimers with anthracene group on the periphery ( $nG[2,2^{n-1},2]-2^{n+1}AN$ ).**

**1G[2,0,2]-4AN:** 0.57 g (1.16 mmol) of 1G[2.0.2]-4Cl dissolved in 25 mL of toluene was slowly added to the solution of 1.07 g (5.13 mmol) anthracene carbinol and 2.5 g (21.5 mmol) of TMEDA in 50 mL of dried toluene. Then, the reaction mixture was warmed to 60 °C for 30 min. The TMEDA·HCl salt was filtered off from the mixture. 1G[2.0.2]-4AN was purified by silica gel chromatography with mixture of chloroform and hexane (2 to 1) removing the excess anthracene. Yield: 1.32 g (87%, 1.10 mmol) as white glassy material.  $^1H$ -NMR (ppm,  $CDCl_3$ ):  $\delta$  -0.45 (s, 6H, SiMe, G0), 0.11 (s, 6H, SiMe, G1), 5.32~5.61 (m, 8H,  $OCH_2$ ), 6.50 (s, 2H, CH=C), 6.88~7.20, 7.20~7.35, 7.82~8.02, 8.02~8.26, 8.26~8.44 (Ph, anthracene).  $^{13}C$ -NMR (ppm,  $CDCl_3$ ):  $\delta$  -4.19 (SiMe, G1), -0.46 (SiMe, G0), 57.43 ( $OCH_2$ ), 124.51, 124.77, 125.79, 126.23, 127.79, 127.91, 128.21, 128.78, 130.29, 130.69, 131.35, 143.93 (Ph, anthracene), 148.47, 159.52 (CH=C). Anal. Calc. for  $C_{80}H_{68}O_4Si_3$  (1177.67): C, 81.59%, H, 5.82%. Found: C, 81.25%, H, 5.82%. UV/Vis.  $\lambda_{max}$  258 nm,  $\epsilon_{max}$   $0.16 \times 10^6$ . GPC: PDI ( $M_w/M_n$ ), 1.00 (783/775); Rt, 19.32 min.

**2G[2,2,2]-8AN:** 0.85 g (0.70 mmol) of 2G[2.2.2]-8Cl and 1.0 g (8.6 mmol) of TMEDA and 1.40 g (6.72 mmol) of anthracene carbinol were used by the same procedure as the above for 1G[2.0.2]-4AN. Yield: 1.68 g (93%, 0.65 mmol) as light yellow to white glassy material.  $^1H$ -NMR (ppm,  $CDCl_3$ ):  $\delta$  -0.56 (s, 6H, SiMe, G0), -0.48 (s, 6H, SiMe, G1), -0.00 (s, 12H, SiMe, G2), 5.09~5.52 (m, 16H,  $OCH_2$ ), 6.21 (s, 2H, CH=C, G1), 6.59 (s, 4H, CH=C (G2)), 6.69~6.82, 6.82~6.96, 6.96~7.13, 7.13~7.51, 7.75~7.93, 7.93~8.20, 8.20~8.45 (Ph, anthracene).  $^{13}C$ -NMR (ppm,  $CDCl_3$ ):  $\delta$  -4.16 (SiMe, G2), -2.62 (SiMe, G0), -0.25 (SiMe, G1), 57.34 ( $OCH_2$ ), 124.46, 124.77, 125.72, 125.89, 126.37, 127.49, 127.58, 127.77, 127.84, 128.70, 130.23, 130.66, 131.31, 143.71 (Ph, anthracene), 145.01, 145.66, 160.65, 163.60 (CH=C). Anal. Calc. for  $C_{176}H_{148}O_8Si_5$  (2587.70): C, 81.69%, H, 5.76%. Found: C, 82.38%, H, 5.72%. UV/Vis.  $\lambda_{max}$  258 nm,  $\epsilon_{max}$   $0.40 \times 10^6$ . GPC: PDI value ( $M_w/M_n$ ), 1.02 (1655/1612); Rt, 18.30 min.

**3G[2,2,2,2]-16AN:** 0.61 g (0.23 mmol) of 3G[2.2.2.2]-16Cl and 1.2 g (10.3 mmol) of TMEDA and 0.92 g (4.42 mmol) of anthracene carbinol were used by the same procedure as the above for 1G[2.0.2]-4AN. Yield: 1.20 g (97%, 0.22 mmol) as yellow glassy material.  $^1H$ -NMR (ppm,  $CDCl_3$ ):  $\delta$  -0.82 ~ -0.48 (m, 24H, SiMe, G0~G2), -0.19~0.11 (m, 24H, SiMe, G3), 5.025.48 (m, 32H,  $OCH_2$ ), 6.01 (s, 2H, CH=C, G1P), 6.18 (s, 4H, CH=C, G2), 6.50 (s, 8H, CH=C, G3), 6.60~6.91, 6.91~7.12, 7.12~7.50, 7.67~7.90, 7.90~8.17, 8.17~8.46 (Ph, anthracene).  $^{13}C$ -NMR (ppm,  $CDCl_3$ ):  $\delta$  -4.17 (SiMe (G3)), -2.77 (SiMe (G2)), -2.29 (SiMe (G1)), -0.16 (SiMe (G0)), 57.30 ( $OCH_2$ ), 124.46, 124.69, 125.69, 125.73, 125.84, 126.38, 127.51, 127.81, 128.68, 130.20, 130.65, 131.28, 142.91, 143.71, 145.11, 145.32 (Ph, anthracene), 144.77, 145.43, 160.54, 160.61, 163.76, 164.90 (CH=C). Anal. Calc. for  $C_{368}H_{308}O_{16}Si_{15}$  (5407.75): C, 81.74%, H, 5.74%. Found: C, 81.47%, H, 5.72%. UV/Vis.  $\lambda_{max}$  258 nm,  $\epsilon_{max}$   $0.83 \times 10^6$ . GPC: PDI value ( $M_w/M_n$ ), 1.04 (5,143/4,935);

Rt, 17.16 min.

**4G[2,2,2,2,2]-32AN:** 0.85 g (0.16 mmol) of 4G[2.2.2.2.2]-32Cl and 0.8 g (6.8 mmol) of TMEDA and 1.29 g (6.18 mmol) of anthracene carbinol were used by the same procedure as the above for 1G[2.0.2]-4AN. Yield: 1.62 g (92%, 0.15 mmol) as light yellow glassy material.  $^1H$ -NMR (ppm,  $CDCl_3$ ):  $\delta$  -0.80 ~ -0.40 (m, 48H, SiMe), -0.19~0.12 (m, 48H, SiMe), 5.00~5.52 (m, 64H,  $OCH_2$ ), 6.01 (s, 2H, CH=C, G1), 6.09 (s, 4H, CH=C, G2), 6.15 (s, 8H, CH=C, G3P), 6.50 (s, 16H, CH=C, G4P), 6.61~6.92, 6.92~7.08, 7.08~7.59, 7.59~7.87, 7.87~8.09, 8.09~8.46 (Ph, anthracene).  $^{13}C$ -NMR (ppm,  $CDCl_3$ ):  $\delta$  -4.18 (SiMe, G4), -2.75 (SiMe, G3), -2.58 (SiMe, G2), -2.34 (SiMe, G1), -0.27 (SiMe, G0), 57.26 ( $OCH_2$ ), 124.41, 124.63, 125.64, 126.08, 126.37, 127.77, 128.62, 130.14, 130.60, 131.21, 142.33, 143.63 (Ph, anthracene), 144.81, 145.27, 160.60, 164.64, 164.79, 165.78 (CH=C). Anal. Calc. for  $C_{752}H_{628}O_{32}Si_{31}$  (11,047): C, 81.76%, H, 5.73%. Found: C, 81.78%, H, 5.71%. UV/Vis.  $\lambda_{max}$  258 nm,  $\epsilon_{max}$   $1.67 \times 10^6$ . GPC: PDI value ( $M_w/M_n$ ), 1.01 (9,843/9,743); Rt, 16.54 min.

**5G[2,2,2,2,2,2]-64AN:** 0.57 g (0.050 mmol) of 5G[2.2.2.2.2.2]-64Cl and 0.41 g of TMEDA (3.56 mmol) and 0.74 g (3.56 mmol) of anthracene carbinol were used by the same procedure as the above for 1G[2.0.2]-4AN. Yield: 1.01 g (91%, 0.045 mmol) as light yellow glassy material.  $^1H$ -NMR (ppm,  $CDCl_3$ ): -0.84 ~ -0.59 (96H, SiMe, G5), -0.32 ~ -0.08 (96H, SiMe, G0~G4), 4.74~5.19 (128H,  $OCH_2$ , G5), 5.84~6.19 (62H, CH=C, G0~G4), 6.32~6.48, 6.48~7.36, 7.36~7.60, 7.60~7.82, 7.82~8.12 (m, 886H, Ph, anthracene).  $^{13}C$ -NMR (ppm,  $CDCl_3$ ):  $\delta$  -4.82 (SiMe, G5), -2.79 (SiMe, G0~G4), 57.61 ( $OCH_2$ ), 122.23, 123.14, 124.66, 125.30, 127.25, 127.80, 128.23, 128.69, 129.04, 130.22, 131.28, 133.54, 134.13, 137.88, 138.61, 143.17 (Ph, anthracene), 144.18, 159.88 (CH=C). Anal. Calc. for  $C_{1520}H_{1268}O_{64}Si_{63}$  (Mw: 22,296): C, 81.80%, H, 5.68%. Found: C, 81.52%, H, 5.66%. UV/Vis.  $\lambda_{max}$  258 nm,  $\epsilon_{max}$   $2.99 \times 10^6$ . GPC: PDI value ( $M_w/M_n$ ), 1.03 (12,675/12,295); Rt, 15.97 min.

**6G[2,2,2,2,2,2,2]-128AN:** 0.58 g (0.025 mmol) of 6G[2.2.2.2.2.2.2]-128Cl and 0.41 g of TMEDA (3.56 mmol) and 0.74 g (3.56 mmol) of anthracene carbinol were used by the same procedure as the above for 1G[2.0.2]-4AN. Yield: 0.99 g (88%, 0.022 mmol) as light yellow glassy material.  $^1H$ -NMR (ppm,  $CDCl_3$ ):  $\delta$  -0.94 ~ -0.56 (192H, SiMe, G6)), -0.58 ~ -0.04 (192H, SiMe, G0~G5), 4.48~5.26 (256H,  $OCH_2$ , G6), 5.84~6.19 (126H, CH=C, G0~G5), 6.22~7.32, 7.32~7.60, 7.60~7.82, 7.82~8.12 (m, 1782H, Ph, anthracene).  $^{13}C$ -NMR (ppm,  $CDCl_3$ ):  $\delta$  -4.87 (SiMe, G6), -2.79 (SiMe, G0~G5), 60.48 ( $OCH_2$ ), 121.83, 123.14, 123.62, 124.78, 127.25, 127.80, 128.70, 130.26, 131.36, 133.55, 134.15, 138.60, 143.00 (Ph, anthracene), 144.18, 159.88 (CH=C). Anal. Calc. for  $C_{3056}H_{2548}O_{128}Si_{127}$  (Mw: 44,824): C, 81.81%, H, 5.68%. Found: C, 81.42%, H, 5.64%. UV/Vis.  $\lambda_{max}$  258 nm,  $\epsilon_{max}$   $5.80 \times 10^6$ . GPC: PDI value ( $M_w/M_n$ ), 1.05 (15,315/14,474); Rt, 15.45 min.

**7G[2,2,2,2,2,2,2,2]-256AN:** 0.44 g (0.095 mmol) of 7G[2.2.2.2.2.2.2.2]-256Cl and 0.31 g of TMEDA (2.69 mmol) and 0.56 g (2.69 mmol) of anthracene carbinol were used by the same procedure as the above for 1G[2.0.2]-4AN. Yield: 0.75 g (88%, 0.083 mmol) as light yellow glassy material.  $^1H$ -NMR

(ppm, CDCl<sub>3</sub>):  $\delta$  -0.98–0.50 (384H, SiMe, G7)), -0.34–0.24 (384H, SiMe, G0–G6), 4.88–5.34 (512H, OCH<sub>2</sub>, G7), 6.00–6.32 (254H, CH=C, G0–G6), 6.32–7.36, 7.52–7.80, 7.80–8.00, 8.00–8.24 (m, 3574H, Ph and anthracene). <sup>13</sup>C-NMR (ppm, CDCl<sub>3</sub>):  $\delta$  -4.82 (SiMe, G7), -2.31 (SiMe, G0–G6), 60.25 (OCH<sub>2</sub>), 122.21, 123.26, 127.24, 127.32, 127.54, 128.67, 130.34, 131.47, 131.85, 134.14, 138.75, 143.00 (Ph, anthracene), 144.00, 163.67 (CH=C). Anal. Calc. for C<sub>6128</sub>H<sub>5108</sub>O<sub>256</sub>Si<sub>255</sub> (Mw: 89,880): C, 81.81%, H, 5.68%. Found: C, 81.39%, H, 5.59%. UV/Vis,  $\lambda_{max}$  258 nm,  $\epsilon_{max}$   $9.79 \times 10^6$ . GPC: PDI ( $M_w/M_n$ ), 1.06 (17,008/16,009); Rt, 15.30 min.

### (3) Preparation and characterization of the dendrimers with benzoxazole groups on the periphery (nG[2,2<sup>n-1</sup>,1]-2<sup>n</sup>BO).

**1G[2,0,1]-2BO:** 0.30 g (0.67 mmol) of 1G[2.0,1]-2Cl in 25 ml of toluene slowly added to the mixed solution of 0.31 g (1.47 mmol) 2-(2-hydroxyphenyl)benzoxazole and 0.17 g (1.45 mmol) of TMEDA in 50 mL of dried toluene at room temperature. Then, the reaction mixture was warmed and kept at 60 °C for 1.5 hrs. The reaction mixture was filtered to remove TMEDA-HCl salt. 1G[2.0,1]-2BO was purified and isolated by silica gel chromatography of chloroform and hexane (3 to 2). Yield: 0.41 g (77%, 0.51 mmol) as yellow glassy material. <sup>1</sup>H-NMR (ppm, CDCl<sub>3</sub>):  $\delta$  -0.47 (s, 6H, SiMe, G0), 0.29 (s, 12H, SiMe, G1), 6.36 (s, 2H, CH=C), 6.80–6.98, 6.98–7.22, 7.22–7.42, 7.42–7.55, 7.70–7.80, 8.04–8.18 (12H, BO, Ph). <sup>13</sup>C-NMR (ppm, CDCl<sub>3</sub>):  $\delta$  -0.75 (SiMe, G1), -0.29 (SiMe, G0), 110.62, 117.37, 119.21, 119.54, 124.96, 125.34, 125.95, 127.07, 127.26, 127.85, 133.52, 139.97, 144.97, 149.09, 158.66, 162.83, 164.05 (Ph, BO). Anal. Calc. for C<sub>48</sub>H<sub>46</sub>N<sub>2</sub>O<sub>4</sub>Si<sub>3</sub> (Mw: 799.16): C, 72.07%, H, 5.75%, N, 3.50%. Found: C, 71.86%, H, 5.57%, N, 3.48%. MALDI-TOF mass: 799.36 (M<sup>+</sup>). UV/Vis,  $\lambda_{max}$  293 nm,  $\epsilon_{max}$   $0.21 \times 10^5$ . GPC: PDI ( $M_w/M_n$ ), 1.01 (682/674); Rt, 19.93 min.

**2G[2,2,1]-4BO:** 0.45 g (0.40 mmol) of 2G[2.2,1]-4Cl and 0.20 g of TMEDA (1.17 mmol) and 0.39 g (1.71 mmol) of 2-(2-hydroxyphenyl)benzoxazole were used by the same procedure as the above for 1G[2.0,1]-2BO. Yield: 0.56 g (76%, 0.30 mmol) as light yellow glassy materials. <sup>1</sup>H-NMR (ppm, CDCl<sub>3</sub>):  $\delta$  -0.71 (s, 6H, SiMe, G0), -0.53 (s, 6H, SiMe, G1), 0.22 (s, 24H, SiMe, G2), 6.04 (s, 12H, CH=C, G0), 6.31 (s, 12H, CH=C, G1), 6.65–6.87, 6.98–7.15, 7.15–7.35, 7.35–7.50, 7.68–7.79, 8.04–8.12 (64H, BO, Ph). <sup>13</sup>C-NMR (ppm, CDCl<sub>3</sub>):  $\delta$  -0.50 (SiMe, G2), -0.29 (SiMe, G0–G1), 110.87, 117.64, 119.77, 125.21, 125.58, 126.14, 127.45, 127.57, 127.63, 127.97, 133.77, 140.24, 144.46, 149.36, 158.95, 163.12 (Ph, BO). Anal. Calc. for C<sub>112</sub>H<sub>104</sub>N<sub>4</sub>O<sub>8</sub>Si<sub>7</sub> (Mw: 1,830): C, 73.44%, H, 5.68%, N, 3.06%. Found: C, 72.90%, H, 5.73%, N, 3.42%. UV/Vis,  $\lambda_{max}$  293 nm,  $\epsilon_{max}$   $0.46 \times 10^5$ . GPC: PDI value ( $M_w/M_n$ ), 1.02 (1,110/1,082); Rt, 18.92 min.

**3G[2,2,2,1]-8BO:** 0.49 g (0.19 mmol) of 3G[2.2,2,1]-8Cl and 0.20 g of TMEDA (1.17 mmol) and 0.37 g (1.75 mmol) of 2-(2-hydroxyphenyl)benzoxazole were used by the same procedure as the above for 1G[2.0,1]-2BO. Yield: 0.58 g (78%, 0.15 mmol) as light yellow glassy material. <sup>1</sup>H-NMR (ppm, CDCl<sub>3</sub>):  $\delta$  -0.80 (s, 12H, SiMe, G2), -0.51 (s, 6H, SiMe, G1), 0.16 (s, 48H, SiMe, G3), 6.07 (s, 6H, CH=C, G0–G1), 6.22 (s, 8H, CH=C, G2), 6.58–6.87, 6.95–7.14, 7.14–7.37, 7.37–7.48, 7.72–7.98, 8.02–8.14 (134H, BO, Ph). <sup>13</sup>C-NMR (ppm,

CDCl<sub>3</sub>):  $\delta$  -2.86 (SiMe, G0–G1), -2.25 (SiMe, G2), -2.22 (SiMe, G3), 110.61, 117.35, 119.18, 119.50, 124.94, 125.31, 125.82, 127.05, 127.33, 127.61, 128.32, 133.51, 137.80, 141.02, 142.79, 144.22, 144.78, 149.05, 158.66, 162.82, 163.74, 164.88 (Ph, BO). Anal. Calc. for C<sub>240</sub>H<sub>220</sub>N<sub>8</sub>O<sub>16</sub>Si<sub>15</sub> (Mw: 3,888): C, 74.00%, H, 5.65%, N, 2.88%. Found: C, 73.24%, H, 5.88%, N, 3.02%. UV/Vis,  $\lambda_{max}$  293 nm,  $\epsilon_{max}$   $0.86 \times 10^5$ . GPC: PDI value ( $M_w/M_n$ ), 1.02 (3,472/3,389); Rt, 17.72 min.

**4G[2,2,2,2,1]-16BO:** 0.32 g (0.061 mmol) of 4G[2,2,2,2,1]-16Cl and 0.12 g of TMEDA (1.17 mmol) and 0.12 g (1.07 mmol) of 2-(2-hydroxyphenyl)benzoxazole were used by the same procedure as the above for 1G[2.0,1]-2BO. Yield: 0.40 g (82%, 0.05 mmol) as light yellow glassy material. <sup>1</sup>H-NMR (ppm, CDCl<sub>3</sub>):  $\delta$  -0.89 (s, 18H, SiMe, G0, G2), -0.81 (s, 12H, SiMe, G3), -0.57 (s, 24H, SiMe, G1), 0.15 (s, 96H, SiMe, G4), 5.94, 5.97 (14H, CH=C, G0–G2), 6.18 (s, 16H, CH=C, G3), 6.54–6.84, 6.90–7.14, 7.14–7.34, 7.34–7.46, 7.66–7.96, 8.02–8.16 (278H, BO, Ph). <sup>13</sup>C-NMR (ppm, CDCl<sub>3</sub>):  $\delta$  -2.87 (SiMe, G0–G3), -0.85 (SiMe, G4), 110.61, 117.35, 119.18, 119.50, 124.94, 125.31, 125.82, 127.05, 127.33, 127.61, 128.32, 133.51, 137.80, 141.02, 142.79, 144.22, 144.78, 149.05, 158.66, 162.82, 163.74, 164.88 (Ph, BO). Anal. Calc. for C<sub>496</sub>H<sub>452</sub>N<sub>16</sub>O<sub>32</sub>Si<sub>31</sub> (Mw: 8,008): C, 74.32%, H, 5.64%, N, 2.79%. Found: C, 73.82%, H, 5.73%, N, 3.21%. UV/Vis,  $\lambda_{max}$  293 nm,  $\epsilon_{max}$   $1.77 \times 10^5$ . GPC: PDI ( $M_w/M_n$ ), 1.00 (5,588/5,562); Rt, 16.84 min.

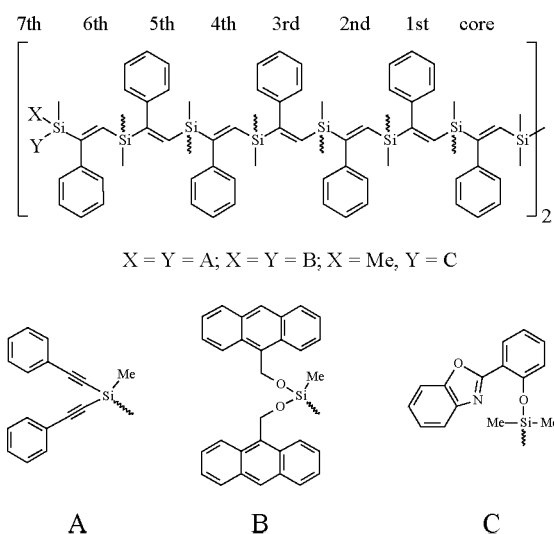
**5G[2,2,2,2,2,1]-32BO:** 0.40 g (0.037 mmol) of 5G-32Cl and 0.14 g of TMEDA (1.19 mmol) and 0.25 g (1.19 mmol) of 2-(2-hydroxyphenyl)benzoxazole were used by the same procedure as the above for 1G[2.0,1]-2BO. Yield: 0.40 g (82%, 0.050 mmol) as yellow glassy material. <sup>1</sup>H-NMR (ppm, CDCl<sub>3</sub>):  $\delta$  -0.96 ~ -0.68 (96H, SiMe, G0–G4), 0.13 (192H, SiMe, G5), 5.79–6.05, 6.12–6.26 (62H, CH=C, G0–G4), 6.50–6.82, 6.82–7.12, 7.12–7.30, 7.30–7.44, 7.62–7.80, 8.00–8.14 (566H, BO, Ph). <sup>13</sup>C-NMR (ppm, CDCl<sub>3</sub>):  $\delta$  -0.44 (SiMe, G5), -0.29 (SiMe, G0–G4), 119.86, 117.64, 119.46, 119.77, 125.21, 125.58, 126.117, 127.331, 127.56, 127.95, 133.77, 140.24, 144.46, 149.35, 158.95, 163.12 (Ph and BO). Anal. Calc. for C<sub>1008</sub>H<sub>916</sub>N<sub>32</sub>O<sub>64</sub>Si<sub>63</sub> (Mw: 16,248): C, 74.44%, H, 5.63%, N, 2.75%. Found: C, 73.99%, H, 5.80%, N, 3.12%. UV/Vis,  $\lambda_{max}$  293 nm,  $\epsilon_{max}$   $3.65 \times 10^5$ . GPC: PDI value ( $M_w/M_n$ ), 1.04 (11,302/10,803); Rt, 15.95 min.

**6G[2,2,2,2,2,2,1]-64BO:** 0.32 g (0.014 mmol) of 6G[2.2,2,2,2,1]-64Cl and 0.12 g of TMEDA (1.06 mmol) and 0.22 g (1.06 mmol) of 2-(2-hydroxyphenyl)benzoxazole were used by the same procedure as the above for 1G[2.0,1]-2BO. Yield: 0.36 g (79%, 0.111 mmol) as yellow glassy material. <sup>1</sup>H-NMR (ppm, CDCl<sub>3</sub>):  $\delta$  -0.96 ~ -0.68 (192H, SiMe, G0–G5), 0.13 (384H, SiMe, G6), 5.68–6.30 (126H, CH=C, G0–G5), 6.50–6.82, 6.82–7.12, 7.12–7.30, 7.30–7.44, 7.62–7.80, 8.00–8.14 (1142H, BO, Ph). <sup>13</sup>C-NMR (ppm, CDCl<sub>3</sub>):  $\delta$  -0.50 (SiMe, G6), -0.29 (SiMe, G0–G5), 110.87, 117.64, 119.47, 119.77, 125.22, 125.59, 127.33, 127.65, 128.44, 127.97, 128.442, 140.25, 144.46, 149.36, 158.96, 163.13 (BO, Ph). Anal. Calc. for C<sub>2032</sub>H<sub>1748</sub>N<sub>64</sub>O<sub>128</sub>Si<sub>127</sub> (Mw: 32,632): C, 74.72%, H, 5.36%, N, 2.74%. Found: C, 73.91%, H, 5.62%, N, 3.04%. UV/Vis,  $\lambda_{max}$  293 nm,  $\epsilon_{max}$   $7.08 \times 10^5$ . GPC: PDI value ( $M_w/M_n$ ), 1.06(12,538/11,775); Rt, 15.53 min.

**7G[2,2,2,2,2,2,2,1]-128BO**: 0.18 g (0.86 mmol) of 7G[2,2,2,2,2,2,2,1]-128Cl and 0.10 g of TMEDA (0.86 mmol) and 0.18 g (0.86 mmol) of 2-(2-hydroxyphenyl)benzoxazole were used by the same procedure as the above for 1G[2,0,1]-2BO. Yield: 0.34 g (83%, 0.0051 mmol) as yellow glassy material.  $^1\text{H-NMR}$  (ppm,  $\text{CDCl}_3$ ):  $\delta$  -1.02 ~ -0.62 (384H, SiMe, G0 ~ G6), 0.32~0.36 (768H, SiMe, G7), 5.82~6.30 (254H, CH=C, G0~G6), 6.30~7.52, 7.60~7.80, 7.94~8.14 (2294H, BO, Ph).  $^{13}\text{C-NMR}$  (ppm,  $\text{CDCl}_3$ ):  $\delta$  -2.39 (SiMe, G0~G6), -0.61 (SiMe, G7), 117.43, 119.27, 119.58, 125.01, 125.39, 125.94, 127.13, 127.67, 133.57, 140.03, 144.28, 149.15, 158.73, 162.91, 164.68 (BO, Ph). Anal. Calc. for  $\text{C}_{408}\text{H}_{3700}\text{N}_{128}\text{O}_{256}\text{Si}_{255}$  (Mw: 65,688): C, 74.53%, H, 5.63%, N, 2.72%. Found: C, 73.86%, H, 5.92%, N, 3.02%. UV/Vis.  $\lambda_{\text{max}}$  293 nm.  $\epsilon_{\text{max}}$   $1.40 \times 10^6$ . GPC: PDI ( $M_w/M_n$ ), 1.01 (14.898/14.623); Rt. 15.30 min.

## Results and Discussion

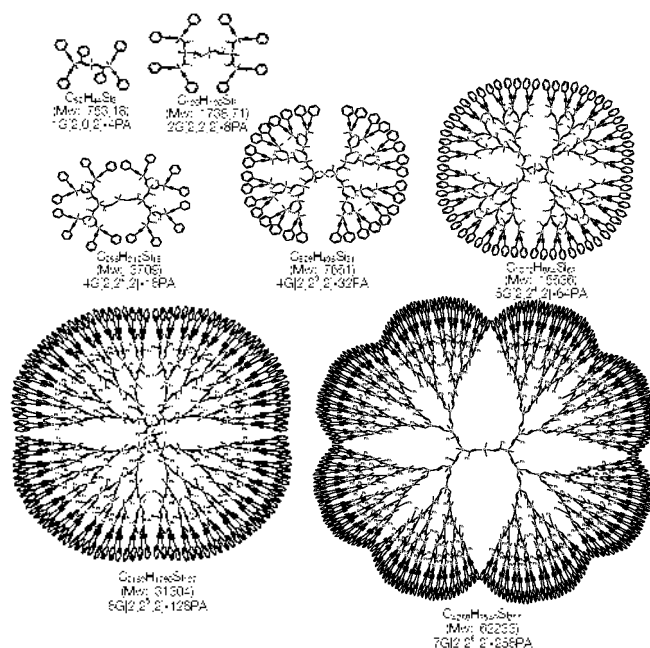
Hydrosilation of bis(phenylacetylenyl)dimethylsilane with two equivalent amounts of dichloromethylsilane gives bis-(2,2-dichloromethylsilyl-2-phenylethenyl)dimethyl silane having four Cl-Si bonds of two peripheral silyl groups. The coupling reaction of the four Cl-Si bonds with lithium phenylacetylide introduces new four phenylacetylenyl groups into the core to give the 2<sup>nd</sup> generation. Hydrosilation of the four acetylene moieties with dichloromethylsilanes to give new Cl-Si bonds and followed by the coupling reaction of the Cl-Si bonds with lithium phenylacetylide are repetitively carried out to obtain the 3<sup>rd</sup> to the 7<sup>th</sup> generation having 256 phenylethenyl groups  $[\text{CH}=\text{C}(\text{Ph})\text{SiMe}]_2$  in inner shells. Lastly instead of lithium phenylacetylide chromophores such as anthracene and benzoxazole are introduced by the coupling reaction of the terminal Cl-Si bonds of each generation with hydroxyl groups of two chromophores.



**Scheme 1.** The skeletal structures of phenylethyne dendrimers and peripheral functions on them. (A) Bis(phenylethyne)methylsilyl, (B) Bis(9-methyloxanthracenyl)methylsilyl, (C) 2-Benzoxazolyl-phenyloxydimethylsilyl group).

**Preparation of phenylethyne dendrimers ( $n\text{G}[2,2^{n-1}, 2]-2^{n+1}\text{PA}$ ; Type A).**<sup>5a, 5b</sup> Cascade type synthetic method is applied to the preparation of phenylethyne dendrimers ( $n\text{G}[2,2^{n-1}, 2]-2^{n+1}\text{PA}$ ,  $n = 1 \sim 7$ ). The first generation (1G[2,0,2]-4Cl) with four growing points of Cl-Si bonds has been prepared by the hydrosilation of bis(phenylacetylenyl)dimethylsilane with two equivalent amount of dichloromethylsilane in the presence of dried platinum metal (10% in active carbon). Sharp single peak from two protons of two double bonds is observed at 6.71 ppm by  $^1\text{H}$  NMR quantitatively. After removing catalyst from the mixture, is isolated the first generation of 1G[2,0,2]-4Cl having air sensitive Cl-Si bonds as light yellow material like gelatin in over 95%. The 2<sup>nd</sup> to the 7<sup>th</sup> generations of  $n\text{G}[2,2^{n-1}, 2]-2^{n+1}\text{Cl}$  ( $n = 2 \sim 7$ ) are prepared in high yield by the same method as the above. The 1<sup>st</sup> generation of 1G[2,0,2]-4PA having four phenylacetylenyl groups,  $\text{Me}_2\text{Si}[\text{CH}=\text{C}(\text{Ph})\text{Si}(\text{Me})(\text{C}\equiv\text{CPh})_2]_2$ , is prepared by the reaction of 1G[2,0,2]-4Cl with four equivalent of lithium phenylacetylide at room temperature. The 1<sup>st</sup> generation of 1G[2,0,2]-4PA is isolated as light yellowish solid in over 90% yield. The 2<sup>nd</sup> generation of 2G[2,2,2]-8PA having 8 phenylacetylenyl groups to the 7<sup>th</sup> generation of 7G[2,2<sup>6</sup>,2]-256PA having 256 phenylacetylenyl groups are prepared by the same method as the above. The reaction rate of the hydrosilation becomes slower with increasing the generation from 1G[2,0,2]-4Cl to 7G[2,2<sup>6</sup>,2]-256Cl.

The dendrimers of  $n\text{G}[2,2^{n-1}, 2]-2^{n+1}\text{PA}$  ( $n = 1 \sim 7$ ; Scheme 2) are quite stable in atmospheric condition, they are identified by  $^1\text{H}$  and  $^{13}\text{C}$  NMR, MALDI-MS, elemental analysis. The purity of the respective dendrimer is confirmed by GPC, in which very narrow peak (polydisperse index value close to unit 1.00) is observed at shorter retention time according to increasing its generation (Fig. 2 and Table 1). Especially



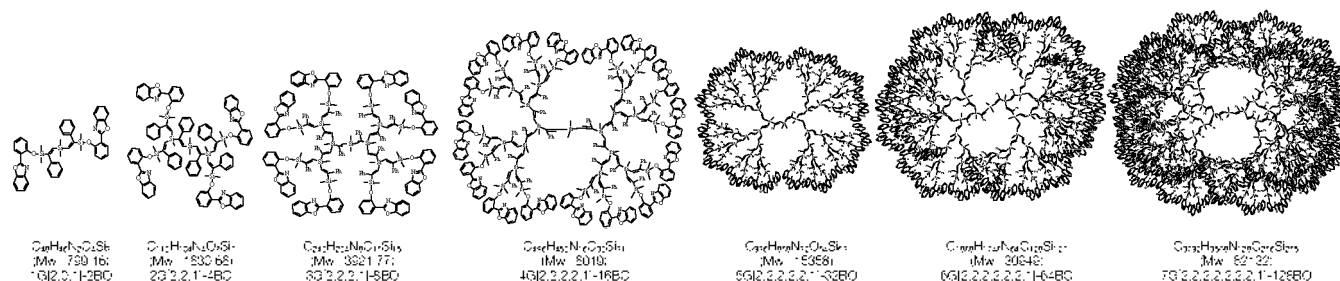
**Scheme 2.** Schematic structures of bis(phenylethyne)methylsilyl substituted dendrimers  $n\text{G}[2,2^{n-1}, 2]-2^{n+1}\text{PA}$  type ( $n = 1 \sim 7$ , 1<sup>st</sup> to 7<sup>th</sup> generation) in plane.

syntheses of 7G[2, 2<sup>6</sup>, 2]-2<sup>8</sup>PA having 256 phenylacetylenyl groups is confirmed unequivocally, but no syntheses of 8G[2, 2<sup>7</sup>, 2]-2<sup>9</sup>PA can be proved by NMR and GPC. It indicates that 7G[2, 2<sup>6</sup>, 2]-2<sup>8</sup>PA can afford enough space for 256 phenylacetylenyl groups, but 8G[2, 2<sup>7</sup>, 2]-2<sup>9</sup>PA have never formed the unified periphery due to its space not enough for 512 phenylacetylenyl groups.

**Preparation of anthracene dendrimers (nG[2, 2<sup>n-1</sup>, 2]- 2<sup>n+1</sup> AN; Type B).**<sup>5c</sup> The 9-anthracenemethoxy groups are introduced into the dendritic periphery by the reaction of Cl-Si bonds of nG[2, 2<sup>n-1</sup>, 2]-2<sup>n+1</sup>Cl (n = 1 ~ 7) with 9-(hydroxymethyl)anthracene in toluene in the presence of TMEDA. After removing TMEDA-HCl salt from the mixture, each dendrimer of nG[2, 2<sup>n-1</sup>, 2]-2<sup>n+1</sup>AN (n = 1 ~ 7) having 9-anthracenemethoxy groups is purified and isolated quantitatively by silica gel-toluene/hexane column chromatography. They have been

characterized by <sup>1</sup>H and <sup>13</sup>C NMR, MALDI mass, GPC, and elemental analysis. From MALDI mass spectrum of the respective dendrimer nG[2, 2<sup>n-1</sup>, 2]-2<sup>n+1</sup>AN (n = 1 to 4) the molecular ion peak of each dendrimer is observed with its characteristic fragmentation ion peaks. GPC of the respective dendrimer nG[2, 2<sup>n-1</sup>, 2]-2<sup>n+1</sup>AN (n = 1 ~ 7) shows very narrow peak with PDI (polydisperse index) value close to 1.00 at shorter retention time according to increasing its generation (Fig. 2). No synthesis of 8G[2, 2<sup>7</sup>, 2]-2<sup>9</sup>AN is proved by GPC chromatography mainly due to its space not enough for 512 9-anthracenemethoxy groups.

**Preparation of benzoxazole dendrimers (nG[2, 2<sup>n-1</sup>, 1]-2<sup>n</sup>BO; Type C).** 2-Benzoxazole-phenyloxy group is bulkier than 9-anthracenemethoxy or phenylacetylenyl group, therefore only one chlorine atom of dichloromethylsilyl group can be substituted by 2-benzoxazolyl-phenyloxy group even at the 1<sup>st</sup>



**Scheme 3.** Schematic structures of (2-benzoxazolyl-2-phenyloxy-dimethylsilyl) substituted dendrimers nG[2, 2<sup>(n-1)</sup>, 1]-2<sup>n</sup>BO type (n = 1 ~ 7, 1<sup>st</sup> to 7<sup>th</sup> generation) in plane.

**Table 1.** Data of GPC and PL for 3 types of dendrimers; nG[2, 2<sup>n-1</sup>, 2]-2<sup>n+1</sup>PA, nG[2, 2<sup>n-1</sup>, 2]-2<sup>n+1</sup>AN, and nG[2, 2<sup>(n-1)</sup>, 1]-2<sup>n</sup>BO (n=1~7)

Dendrimers <sup>a</sup> (No of Functions)	Formula (M <sub>w</sub> )	GPC <sup>b</sup> PDI(M <sub>w</sub> /M <sub>n</sub> )/Rt (min)	PL <sup>c</sup> λ <sub>max</sub> (nm)	R <sup>d</sup>
1G[2,2]-4PA	C <sub>52</sub> H <sub>44</sub> Si <sub>3</sub> (753.2)	1.01(753.739)/19.66	418	
2G[2,2,2]-8PA	C <sub>120</sub> H <sub>100</sub> Si <sub>7</sub> (1738)	1.01(1209.1188)/18.76	418	
3G[2,2,2,2]-16PA	C <sub>256</sub> H <sub>212</sub> Si <sub>15</sub> (3709)	1.03(3166.3069)/17.25	418	
4G[2,2,2,2,2]-32PA	C <sub>528</sub> H <sub>436</sub> Si <sub>31</sub> (7651)	1.04(5292.5075)/16.35	418	
5G[2,2,2,2,2,2]-64PA	C <sub>1072</sub> H <sub>884</sub> Si <sub>63</sub> (15536)	1.04(11226.10709)/16.02	418	
6G[2,2,2,2,2,2,2]-128PA	C <sub>2160</sub> H <sub>1780</sub> Si <sub>127</sub> (31304)	1.07(14747.13774)/15.54	418	
7G[2,2,2,2,2,2,2,2]-256PA	C <sub>4288</sub> H <sub>3540</sub> Si <sub>255</sub> (62233)	1.05(17109.16165)/15.15	418	
1G[2,2]-4AN	C <sub>80</sub> H <sub>68</sub> O <sub>4</sub> Si <sub>3</sub> (1177)	1.00(783.775)/19.32	349,415,439	
2G[2,2,2]-8AN	C <sub>176</sub> H <sub>148</sub> O <sub>8</sub> Si <sub>7</sub> (2587)	1.02(1655.1612)/18.30	349,415,439	
3G[2,2,2,2]-16AN	C <sub>368</sub> H <sub>308</sub> O <sub>16</sub> Si <sub>15</sub> (5407)	1.04(5143.4935)/17.16	349,415,439	
4G[2,2,2,2,2]-32AN	C <sub>752</sub> H <sub>628</sub> O <sub>32</sub> Si <sub>31</sub> (11048)	1.01(9843.9743)/16.54	349,415,439	
5G[2,2,2,2,2,2]-64AN	C <sub>1520</sub> H <sub>1268</sub> O <sub>64</sub> Si <sub>63</sub> (22328)	1.03(12675.12295)/15.97	349,415,439	
6G[2,2,2,2,2,2,2]-128AN	C <sub>3056</sub> H <sub>2548</sub> O <sub>128</sub> Si <sub>127</sub> (44888)	1.05(15315.14474)/15.45	349,415,439	
7G[2,2,2,2,2,2,2,2]-256AN	C <sub>6128</sub> H <sub>5108</sub> O <sub>256</sub> Si <sub>255</sub> (90009)	1.06(17008.16009)/15.30	349,415,439	
1G[2,1]-2BO	C <sub>48</sub> H <sub>8</sub> N <sub>2</sub> O <sub>4</sub> Si <sub>3</sub> (799.2)	1.01(682.674)/19.93	475	
2G[2,2,1]-4BO	C <sub>112</sub> H <sub>104</sub> N <sub>4</sub> O <sub>8</sub> Si <sub>7</sub> (1830)	1.02(1110.1082)/18.92	475	
3G[2,2,2,1]-8BO	C <sub>242</sub> H <sub>224</sub> N <sub>8</sub> O <sub>16</sub> Si <sub>15</sub> (3921)	1.02(3472.3389)/17.72	475	
4G[2,2,2,2,1]-16BO	C <sub>496</sub> H <sub>452</sub> N <sub>16</sub> O <sub>32</sub> Si <sub>31</sub> (8019)	1.00(5588.5562)/16.84	357/475	T
5G[2,2,2,2,2,1]-32BO	C <sub>926</sub> H <sub>868</sub> N <sub>32</sub> O <sub>64</sub> Si <sub>63</sub> (15358)	1.04(11302.10803)/15.95	357	
6G[2,2,2,2,2,2,1]-64BO	C <sub>1838</sub> H <sub>1748</sub> N <sub>64</sub> O <sub>128</sub> Si <sub>127</sub> (30950)	1.06(12538.11775)/15.53	357	
7G[2,2,2,2,2,2,2,1]-128BO	C <sub>3592</sub> H <sub>3508</sub> N <sub>128</sub> O <sub>256</sub> Si <sub>255</sub> (62132)	1.01(14898.14623)/15.3	357	

<sup>a</sup>PA: Phenylethynylsilane terminated dendrimer, AN: Anthracene terminated dendrimer, BO: Benzoxazole terminated dendrimer. <sup>b</sup>GPC: Gel Permeation Chromatography, <sup>c</sup>PL: Photoluminescence, dendrimers with anthracene (AN) have three maximal peaks. <sup>d</sup>T: Dendrimers show blue shift in PL data.

generation of 1G[2.0,1]-2Cl. Therefore another dendrimer of  $nG[2.2^{n-1},1]-2^nCl$  ( $n = 1 \sim 7$ ) (type C) is designed and prepared by the hydrosilation of phenylacetylenyl group with dimethylchlorosilane instead of dichloromethylsilane. One 2-benzoxazole-phenoxy group is substituted on each silicon atom of the dendrimer  $nG[2.2^{n-1},1]-2^nCl$  ( $n = 1 \sim 7$ ) by the reaction of Cl-Si bond with 2-(2-hydroxyphenyl)benzoxazole in the presence of TMEDA. From the reaction mixture dendrimer of  $nG[2.2^{n-1},1]-2^nBO$  ( $n = 1 \sim 7$ ) is purified and isolated quantitatively by silica gel-toluene chromatography. Each dendrimer is characterized by  $^1H$  and  $^{13}C$  NMR, MALDI-MS, and elemental analysis. All dendrimers of  $nG[2.2^{n-1},1]-2^nBO$  (Scheme 3) are soluble in organic solvent such as toluene, diethyl ether, and chloroform. The molecularity of the respective dendrimer  $nG[2.2^n,1]-2^nBO$  ( $n = 1 \sim 7$ ) is determined by GPC, in which very narrow peak with PDI value close to 1.00 at shorter retention time according to increasing its generation (Fig. 2).

**Measurements of the unified properties for carbosilane dendrimers:** For the preparation and identification of higher generation dendrimer it has been very critical and controversial to measure its unimolecularity or purity. The MALDI mass spectroscopy provides valuable information for the unimolecularity of lower generation dendrimer; nonetheless generally it gives no conclusive information for its purity. Therefore in this work GPC has been chosen to study the molecularity of the dendrimer of  $nG[2.2^{n-1},2]-2^{n+1}PA$  ( $n = 1 \sim 7$ ) (Fig. 1 and Table 1).

The GPC chromatogram in Fig. 1 shows very narrow peaks corresponding to the respective generation of the dendrimers. As same as linear polymers, the peak of heavier dendrimer comes first in GPC. The first peak from left is that of the highest generation dendrimer, 7G[2.2<sup>6</sup>,2]-2<sup>7</sup>PA, and the last peak from left is that of the lowest generation dendrimer, 1G[2.0,2]-2<sup>2</sup>PA. Most significant feature of the chromatogram is that each peak has no shoulder in the left and the right side of the peak for the 1<sup>st</sup> to the 5<sup>th</sup> generation dendrimers in Figure 1 and 2. On the other hand for the 6<sup>th</sup> and/or 7<sup>th</sup> generation of them a little shoulder can be recognized in the only left side of each peak. The shoulder in the left side of the peak must be come from the corresponding dendrimer having impurities, which are stuck between its branches. It is plausible that higher generation dendrimer has more space to capture any impurity between its branches. Nevertheless no shoulder in the right side of each peak is observed, it indicates that the purified each dendrimer has no structural defect on its branches or periphery.

In addition the PDI values of the peaks are very close to 1.00 in the range from 1.00 to 1.07. It indicates that the calculated molecular weight from GPC is very little greater than that of the dendrimer with no defect ( $M_n \geq M_w$ ). From these results it seems to be reasonable that the closer to 1.00 the PDI value of dendrimer is observed, the purer dendrimer is obtained. However, in the preparation of the 8<sup>th</sup> generation 8G[2.2<sup>7</sup>,2]-2<sup>8</sup>PA no narrow peak in GPC chromatogram is observed.

In conclusion, three types of dendrimer,  $nG[2.2^{n-1},2]-2^{n+1}PA$  for phenylethynyl group substituted dendrimer,  $nG[2.2^{n-1},$

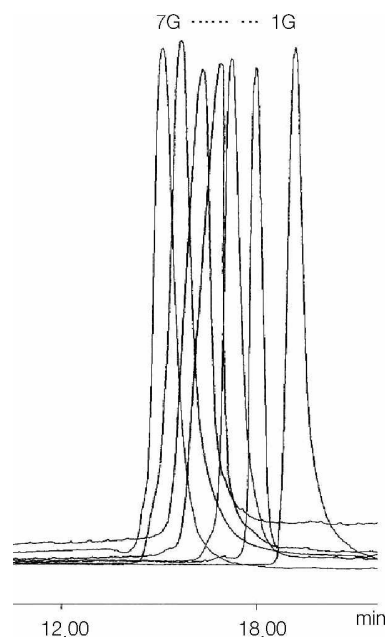


Figure 1. GPC diagram for phenylethynylsilane terminated dendrimers  $nG[2.2^{n-1},2]-2^{n+1}PA$  ( $n = 1 \sim 7$ )

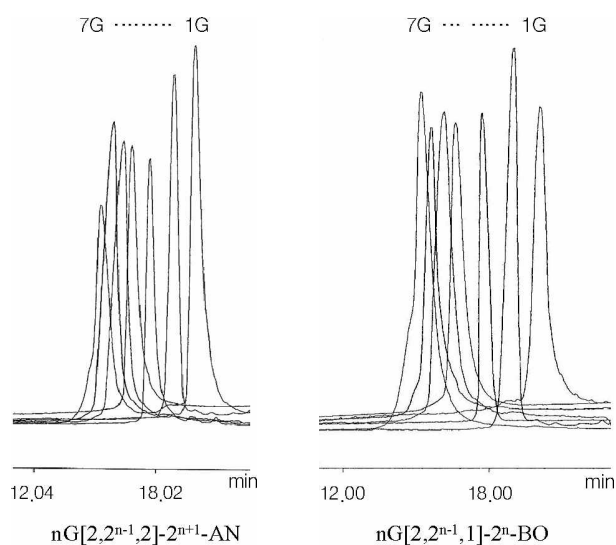
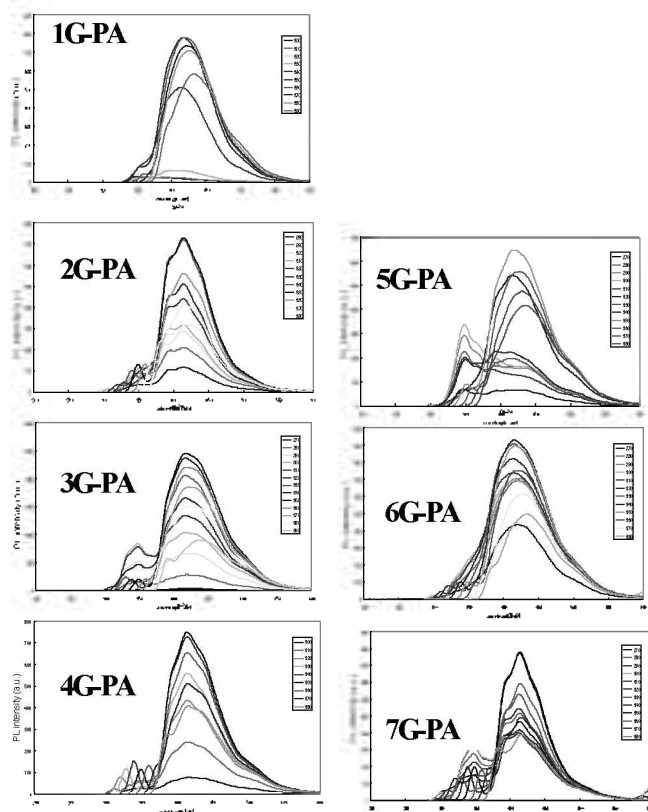


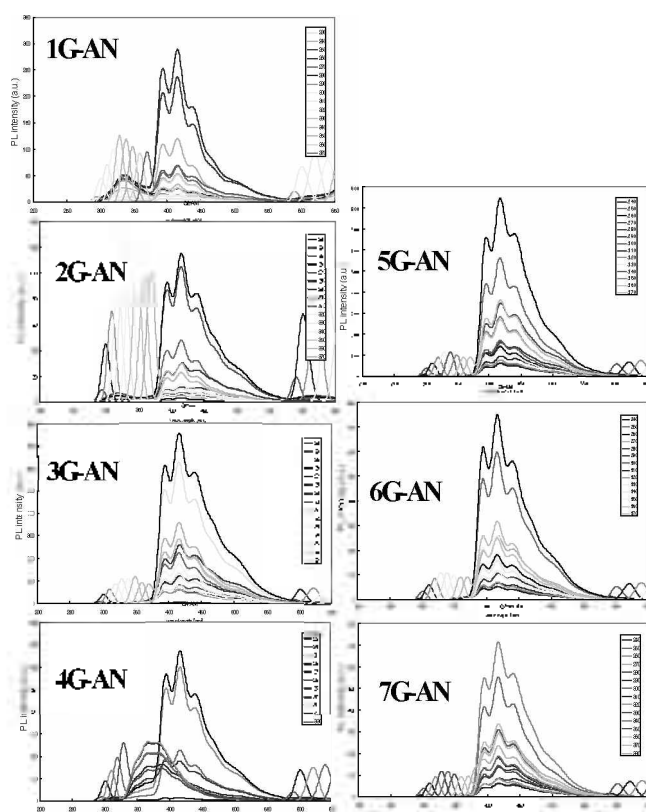
Figure 2. GPC diagram for anthracene terminated dendrimers  $nG[2.2^{n-1},2]-2^{n+1}AN$  ( $n = 1 \sim 7$ )(left) and benzoxazole terminated dendrimers  $nG[2.2^{n-1},1]-2^nBO$  ( $n = 1 \sim 7$ )(right).

$2]-2^{n+1}AN$  for 9-anthracenemethoxy group substituted dendrimer, and  $nG[2.2^{n-1},1]-2^nBO$  for 2-benzoxazole-phenoxy group substituted dendrimer, have synthesized up to the 7<sup>th</sup> generation, after which no enough space seems to be available for the incoming 2-benzoxazole-phenoxy group on the periphery.

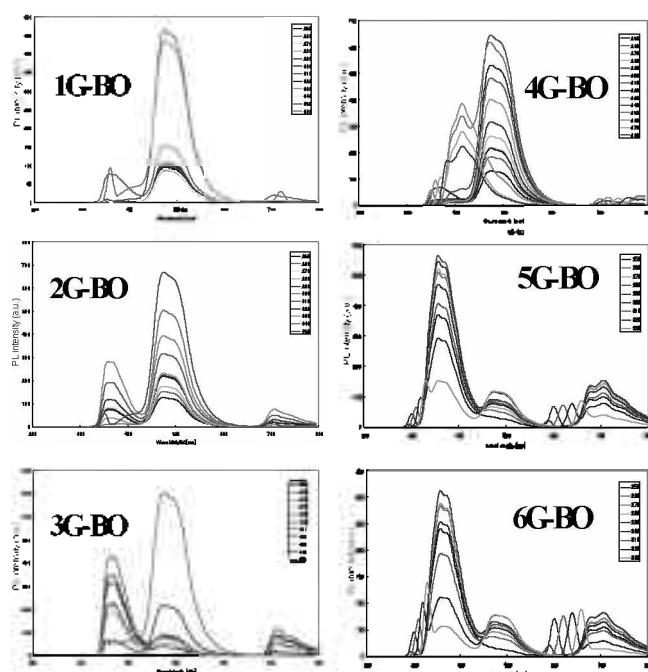
**Measurements of photoluminescent properties of the dendrimers:** The PL spectra of  $nG[2.2^{n-1},2]-2^{n+1}PA$  ( $n = 1 \sim 7$ ) show one  $\lambda_{max}$  at the wavelength of 418 nm (Figure 3). The PL spectra of  $nG[2.2^{n-1},2]-2^{n+1}AN$  ( $n = 1 \sim 7$ ) show three  $\lambda_{max}$  at the wavelength of 349, 415, and 439 nm, those are charac-



**Figure 3.** Photoluminescent spectra of the dendrimers substituted by phenylethynyl group  $nG[2,2^{n-1},2]-2^{n+1}PA$  ( $n = 1 \sim 7$ ).

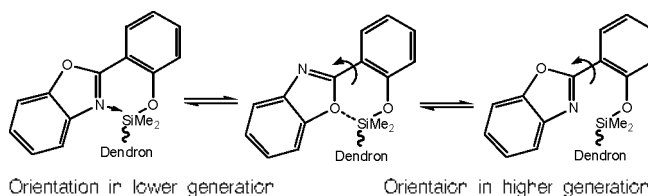


**Figure 4.** Photoluminescent spectra of dendrimers substituted by anthracenemethoxy group  $nG[2,2^{n-1},2]-2^{n+1}AN$  ( $n = 1 \sim 7$ ).



**Figure 5.** Photoluminescent spectra of dendrimers substituted by 2-bezoxazole-phenoxy group  $nG[2,2^{n-1},1]-2^nBO$  ( $n = 1 \sim 6$ ).

teristic peaks of anthracene (Figure 4). With increasing generation of the dendrimer the absorption of  $\lambda_{max}$  shows no significant change, the intensity of  $\lambda_{max}$  simply depends on the



**Scheme 4.** Suggested mechanism for blue-shift of  $nG[2,2^{n-1},1]-2^nBO$  dendrimers.

numbers of chromophores attached to the dendrimer. It indicates that the number of peripheral triple and double bonds inside dendrimer has no influence on PL spectrum of the dendrimer.

The PL spectra of  $nG[2,2^{n-1},1]-2^nBO$  ( $n = 1 \sim 6$ ) show one smaller  $\lambda_{max}$  at the wavelength of 347 and the other bigger  $\lambda_{max}$  at the wavelength of 475 nm. Unexpectedly the intensity of the smaller  $\lambda_{max}$  at the wavelength of 347 nm is increased and the intensity of the bigger  $\lambda_{max}$  at the wavelength of 475 nm is decreased with increasing the generation of  $nG[2,2^{n-1},1]-2^nBO$ , from the 1<sup>st</sup> to the 6<sup>th</sup> generation. In the end the intensity of  $\lambda_{max}$  at the wavelength of 347 nm is bigger than that of  $\lambda_{max}$  at the wavelength of 475 nm for the 5<sup>th</sup> and the 6<sup>th</sup> generation of  $nG[2,2^{n-1},1]-2^nBO$  ( $n = 5, 6$ ). It is plausible that the space around Si atom becomes smaller with increasing the generation. For the lower generation dendrimer there is enough space around Si atom for the bulky 2-bezoxazolephenoxy group to be planar geometry, in which nitrogen as well as oxygen atoms of the 2-bezoxazole-phenoxy group can coordinate



equatorially to Si atom. However for the higher generation dendrimer 2-benzoxazole-phenoxy group is too bulky to move around Si atom, therefore the benzoxazole and phenyl groups rotate to minimize their bulkiness (Scheme 4).

**Acknowledgments.** This work was supported by grant No (R01-2006-000-11120-0) from the Basic Research Program Korea Science and Engineering Foundation of Ministry of Science & Technology and personally supported by Korean Research Foundation (KRF-2006-351-C00015).

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