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 1st generation. The same hydrosilation and alkylation are repeated to obtain the 7th 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 1st to the 7th generations, the 7th generation of each dendrimer has 256 phenylethynyl, 256 9-anthracenemethoxy, or 128 2-(2-phenoxy)benzoxazole groups. Each synthesized dendrimer is unequivocally characterized by $^1$H and $^{13}$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-anthracenemethoxy group substituted dendrimers show no significant change with increasing the generation from the 1st to the 7th. However, the PL spectra of 2-(2-phenoxy)benzoxazole group substituted dendrimers show a blue-shift trend with increasing the generation from the 1st to the 7th.

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

Introduction

Since Vögtle reported the first cascade synthesis of new homologous dendritic molecules have been prepared. 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. 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. For lower generation dendrimer, the molecular weight of which is around thousands Dalton, the unimolecularity has been confirmed by mass spectroscopy. 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. In this reason GPC (The gel permeation chromatography) is used to determine the unimolecularity of dendrimer.

Herein, novel carbosilane dendrimers (1st to 7th generation), having chromophores of phenylethynyl, antracenyl, and benzoxazolyl groups on the periphery, are synthesized and characterized by $^1$H and $^{13}$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 (Ultrastyragel 0.78 x 30 cm; 10^3, 10^4 and 10^5), 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\(^{m+1}\),1]\(-2^n\)X and nG[2,2\(^{m+1}\),2]\(-2^{n+1}\)X; the n\(^{th}\)G refers to generation number, the first 2 in bracket refers to the number of branches in core, the 2\(^{m+1}\) 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 2X or 2\(^{n+1}\)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.

Dichloromethylsilane is used for the hydrosilation of the preparation of nG[2,2\(^{m+1}\),2]\(-2^{n+1}\)PA and nG[2,2\(^{m+1}\),2]\(-2^{n+1}\)AN,
chlorodimethylsilane is used for the hydrosilation of the preparation of \(\text{ng}[2,2^\text{m},1]^{-2}\text{BO}\).

(1) **Synthesis of \text{ng}[2,2^\text{m},1]^{-2}\text{PA}** type dendrimers.

\(\text{1G}[2,0,2]-4\text{PA}\): 55 mL (55 mmol) of lithium phenylacetylide (1 M in THF) was added to the solution of 5.65 g (11.52 mmol) of \(\text{1G}[2,0,2]-4\text{Cl}\) 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. \(\text{1G}[2,0,2]-4\text{PA}\) 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. 

\(\text{1H-NMR (ppm, CDCl}_3): \) δ -0.88, -0.84, -0.83 (s, 48H, SiMe, G0-G3), 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). \(\text{13C-NMR (ppm, CDCl}_3): \) δ -3.26 (SiMe, G0-G2), -1.10 (SiMe, G3), -0.80 (SiMe, G4), 89.16, 107.48 (C=C), 142.82, 144.49, 154.34, 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 \(\text{C}_{3528}\text{H}_{212}\text{Si}_{15}\): C, 82.93%, H, 5.70%. Found: C, 81.99%, H, 5.79%. MALDI-TOF mass: 7754.63 (M+Na)+. UV/Vis, \(\epsilon_{\text{max}}\) 253 nm, \(\epsilon_{\text{max}}\) 4.47 × 10^5. GPC: PDI (M_{w}/M_{n}), 1.04 (5.292/5.075); Rt, 16.35 min.

\(\text{5G}[2,2^\text{m},1]^{-32}\text{PA}\): 3.0 g (0.26 mmol) of \(\text{5G}[2,2^\text{m},1]^{-32}\text{Cl}\) and 20 mL (20 mmol) of lithium phenylacetylide were used by the same procedure as the above for \(\text{1G}[2,0,2]-4\text{PA}\). The mixture refluxed for 10 hrs. Yield: 3.22 g (79%, 0.20 mmol) as yellow glassy material. 

\(\text{1H-NMR (ppm, CDCl}_3): \) 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-G6). \(\text{13C-NMR (ppm, CDCl}_3): \) δ -3.31 (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 \(\text{C}_{3102}\text{H}_{232}\text{Si}_{15}\): C, 82.93%, H, 5.70%. Found: C, 82.65%, H, 5.43% UV/Vis, \(\epsilon_{\text{max}}\) 253 nm, \(\epsilon_{\text{max}}\) 1.86 × 10^5. GPC: PDI (M_{w}/M_{n}), 1.04 (11,226/10,709); Rt, 16.02 min.

\(\text{3G}[2,2^\text{m},1]^{-32}\text{PA}\): 4.79 g (1.87 mmol) of \(\text{3G}[2,2^\text{m},1]^{-32}\text{Cl}\) and 20 mL (20 mmol) of lithium phenylacetylide were used by the same procedure as the above for \(\text{1G}[2,0,2]-4\text{PA}\). The mixture refluxed for 10 hrs. Yield: 3.00 g (74%, 0.095 mmol) as yellow glassy material. 

\(\text{1H-NMR (ppm, CDCl}_3): \) δ -0.96 ~ -0.60 (126H, SiMe, G0-G5), 0.20-0.49 (126H, SiMe, G6), 5.82-6.14 (126H, CH=C, G0-G5), 6.50-7.68 (1270H, Ph, G0-G6). \(\text{13C-NMR (ppm, CDCl}_3): \) 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-G6), 122.63, 126.49, 127.60, 128.05, 128.20, 128.83, 132.03, 163.38 (Ph, G0-G6). Anal. Calc. for \(\text{C}_{2580}\text{H}_{1780}\text{Si}_{127}\): C, 82.93%, H, 5.69% Found: C, 82.26%, H, 5.43% UV/Vis, \(\epsilon_{\text{max}}\) 253 nm, \(\epsilon_{\text{max}}\) 4.47 × 10^5 GPC: PDI (M_{w}/M_{n}), 1.07 (14,747/13,774); Rt, 15.54 min.

\(\text{5G}[2,2^\text{m},1]^{-32}\text{PA}\): 1.00 g (0.022 mmol) of \(\text{5G}[2,2^\text{m},1]^{-32}\text{Cl}\) and 7 mL (7 mmol) of lithium phenylacetylide were used by the same procedure as the above for \(\text{1G}[2,0,2]-4\text{PA}\). The mixture refluxed for 10 hrs. Yield: 1.08 g (82%, 0.017 mmol) as yellow glassy material.
× 10^6. GPC: PDI value (Mw/Mn), 1.05 (17,109/16,165); Rt, 15.15 min.

(2) Preparation and characterization of the dendrimers with anthrancene group on the periphery (nG[2,2,1,2]-2n+1AN).

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) anthrance 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-CHCl salt was filtered off from the mixture. 1G[2,0,2]-4AN was purified by silica gel chromatography with mixture of chlororom and hexane (2 to 1) removing the excess anthra-cene. Yield: 1.32 g (87%, 1.10 mmol) as white glassy ma-
"
(ppm, CDCl₃): δ -0.98~0.50 (384H, SiMe, G7)). -0.34~0.24 (384H, SiMe, G0~G6). 4.88~5.34 (512H, OCH₂, G7). 6.00~6.32 (254H, CH=C, G0~G6). 6.32~7.76. 7.52~7.80. 7.80~8.00. 8.00~8.24 (m, 3574H, Ph and anthracene). 13C-NMR (ppm, CDCl₃): δ -4.82 (SiMe, G7). -2.51 (SiMe, G0~G6), 60.25 (OCH₂). 122.21, 123.26, 127.24, 127.32, 127.54, 128.67, 130.34, 131.47, 131.85, 134.14, 138.75, 140.00 (Ph, anthracene). 144.00, 163.67 (CH=C). Anal. Calc. for C₆₁₁H₅₁₀O₈Si₁₀ (Mw: 89,880): C, 81.81%. H, 5.68%. Found: C, 81.39%, H, 5.59%. UV/Vis, λmax 293 nm, εmax 876, Vol. 30, No. 4 Chungkyun Kim et al.

5G[2,2,2,1]-16BO: 0.32 g (0.061 mmol) of 4G[2,2,2,1]-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%, 0.055 mmol) as yellow gelatinous material. 1H-NMR (ppm, CDCl₃): δ -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). 13C-NMR (ppm, CDCl₃): δ -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, 126.21, 126.82, 135.11, 137.40, 141.02, 142.79, 144.22, 147.78, 149.05, 158.66, 162.82, 163.74, 164.88 (Ph, BO). Anal. Calc. for C₄₄₅H₃₅₂N₂O₄Si₂₀ (Mw: 8,008): C, 74.32%, H, 5.64%, N, 2.79%. Found: C, 73.82%, H, 5.73%, N, 3.21%. UV/Vis, λmax 293 nm, εmax 1.77 × 10⁵. GPC: (M₀/Mₙ), 1.00 (5,588/5,562); Rt, 16.84 min.

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. 1H-NMR (ppm, CDCl₃): δ -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). 13C-NMR (ppm, CDCl₃): δ -2.86 (SiMe, G0~G1). -2.25 (SiMe, G2). -2.22 (SiMe, G3). 110.61, 117.35, 119.19, 119.50, 124.94, 125.31, 125.82, 127.05, 127.33, 126.21, 126.82, 135.11, 137.40, 141.02, 142.79, 144.22, 147.78, 149.05, 158.66, 162.82, 163.74, 164.88 (BO, Ph). Anal. Calc. for C₄₄₅H₃₅₂N₂O₄Si₂₀ (Mw: 3,888): C, 74.00%, H, 5.65%, N, 2.88%. Found: C, 73.24%, H, 5.88%, N, 3.02%. UV/Vis, λmax 293 nm, εmax 0.86 × 10⁵. GPC: (M₀/Mₙ), 1.02 (3,472/3,369); Rt, 17.72 min.
7G[2,2,2,2,2,2,1]-128BO: 0.18 g (0.86 mmol) of 7G[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.

1H-NMR (ppm, CDCl3): δ -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).

13C-NMR (ppm, CDCl3): δ -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 C4288H3540Si255 (Mw: 62223): C, 74.52%, H, 5.63%, N, 2.72%. Found: C, 73.86%, H, 5.92%, N, 3.02%. UV/Vis, λmax 293 nm, λ293 nm, εmax 1.40 x 10^4. GPC: (Mn/Ma), 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-dichloromethyl-2-phenylthienyl)dimethylsilane 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 2nd 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 3rd to the 7th generation having 256 phenylacetylenyl groups [CH = C(Ph)SiMe]- 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.

Preparation of phenylethynylsilane dendrimers nG[2,2n+1, 2]-2nPA; Type A. S2, S5th Cascade type synthetic method is applied to the preparation of phenylethynylsilane dendrimers nG[2,2n+1, 2]-2nPA, n = 2 - 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(phenylacetylene)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 1H NMR quantitatively. After removing catalyst from the mixture, is isolated the first generation 1G[2,0,2]-4Cl having air sensitive Cl-Si bonds as light yellow material like gelatin in over 95%. The 2nd to the 7th generations of nG[2,2n+1, 2]-2nPA (n = 2 - 7) are prepared in high yield by the same method as the above. The 1st generation 1G[2,0,2]-4PA having four phenylacetylenyl groups, Me3Si[CH=C(Ph)Si(Me)(C≡CPh)]2, is prepared by the reaction of 1G[2,0,2]-4Cl with four equivalent of lithium phenylacetylide at room temperature. The 1st generation 1G[2,0,2]-4PA is isolated as light yellowish solid in over 90% yield. The 2nd generation of 2G[2,2,2]-8PA having 8 phenylacetylenyl groups to the 7th generation of 7G[2,2,2]-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[2,2,2]-256Cl.

The dendrimers of nG[2,2n+1, 2]-2nPA (n = 1 - 7; Scheme 2) are quite stable in atmospheric condition, they are identified by 1H and 13NMR, 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 1](https://example.com/scheme1.png)

**Scheme 1.** The skeletal structures of phenylethynylsilane dendrimers and peripheral functions on them. (A) Bis(phenylethynyl)methylsilyl, (B) Bis(9-methoxynaphthaceny1)methylsilyl, (C) 2-Benzoxazolylphenoxymethylsilyl group.

![Scheme 2](https://example.com/scheme2.png)

**Scheme 2.** Schematic structures of bis(phenylethynyl)methylsilyl substituted dendrimers nG[2,2n+1, 2]-2nPA type (n=1-7, 1st to 7th generation) in plane.
syntheses of 7G[2, 2^e,2]-2^ePA having 256 phenylacetylenyl groups is confirmed unequivocally, but no syntheses of 8G[2, 2^f,2]-2^fPA can be proved by NMR and GPC. It indicates that 7G[2, 2^e,2]-2^ePA can afford enough space for 256 phenylacetylenyl groups, but 8G[2, 2^f,2]-2^fPA have never formed the unified periphery due to its space not enough for 512 phenylacetylenyl groups.

**Preparation of anthracene dendrimers (nG[2, 2^n,2]-2^n+1 AN; Type B).** The 9-anthracemethoxy groups are introduced into the dendritic periphery by the reaction of Cl-Si bonds of nG[2, 2^n,2]-2^n+1Cl (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^n,2]-2^n+1AN (n = 1 ~ 7) having 9-anthracemethoxy groups is purified and isolated quantitatively by silica gel-toluene/hexane column chromatography. They have been characterized by ^1H and ^13C NMR, MALDI mass, GPC, and elemental analysis. From MALDI mass spectrum of the respective dendrimer nG[2, 2^n,2]-2^n+1AN (n = 1 ~ 4) the molecular ion peak of each dendrimer is observed with its characteristic fragmentation ion peaks. GPC of the respective dendrimer nG[2, 2^n,2]-2^n+1AN (n = 1 ~ 7) shows very narrow peak with PDI (polydispersity index) value close to 1.00 at shorter retention time according to increasing its generation (Fig. 2). No synthesis of 8G[2, 2^f,2]-2^fPA is proved by GPC chromatography mainly due to its space not enough for 512 9-anthracemethoxy groups.

**Preparation of benzoazole dendrimers (nG[2, 2^n,1]-2^nBO; Type C).** 2-Benzoxazole-phenolxy group is bulkier than 9-anthracemethoxy or phenylacetylenyl group, therefore only one chlorine atom of dichloromethylsilyl group can be substituted by 2-benzoxazoyl-phenolxy group even at the 1st generation.

**Scheme 3.** Schematic structures of (2-benzoazolyl-2-phenolxydimethylsilyl substituted dendrimers nG[2, 2^n,1]-2^nBO type (n = 1 ~ 7, 1st to 7th generation) in plane.

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

<table>
<thead>
<tr>
<th>Dendrimers^a</th>
<th>Formula</th>
<th>GPC^b</th>
<th>PL^c</th>
<th>R^d</th>
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<td>(No of Functions)</td>
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<td>M_M / PDI (Rt min)</td>
<td>λ_max (nm)</td>
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<td>1G[2,1]-1BO</td>
<td>C_{28}H_{28}O (799.2)</td>
<td>1.01(682/674)</td>
<td>19.93</td>
<td>475</td>
</tr>
<tr>
<td>2G[2,1]-4BO</td>
<td>C_{28}H_{56}O (1830)</td>
<td>1.02(1110/1082)</td>
<td>18.92</td>
<td>475</td>
</tr>
<tr>
<td>3G[2,1,1]-8BO</td>
<td>C_{28}H_{110}O (3921)</td>
<td>1.02(3472/3389)</td>
<td>17.72</td>
<td>475</td>
</tr>
<tr>
<td>4G[2,2,2,1,1]-16BO</td>
<td>C_{28}H_{22}O (8019)</td>
<td>1.06(5558/5562)</td>
<td>16.84</td>
<td>357/475</td>
</tr>
<tr>
<td>5G[2,2,2,2,1,1]-32BO</td>
<td>C_{28}H_{34}O (15358)</td>
<td>1.04(11302/10803)</td>
<td>15.95</td>
<td>357</td>
</tr>
<tr>
<td>6G[2,2,2,2,2,1]-64BO</td>
<td>C_{105}H_{84}O (30950)</td>
<td>1.06(12538/11775)</td>
<td>15.53</td>
<td>357</td>
</tr>
<tr>
<td>7G[2,2,2,2,2,2,1]-128BO</td>
<td>C_{123}H_{106}O (62132)</td>
<td>1.01(1499/1462)</td>
<td>15.33</td>
<td>357</td>
</tr>
</tbody>
</table>

^aPA; Phenylethynylsilane terminated dendrimer, AN; Anthracene terminated dendrimer, BO; Benzoazole terminated dendrimer, ^bGPC; Gel Permeation Chromatography, ^cPL; Photoluminescence, dendrimers with anthracene (AN) have three maximal peaks, ^dT; Dendrimers show blue shift in PL data.
generation of 1G[2,0,1]-2Cl. Therefore another dendrimer of nG[2,2n-1,1]-22Cl (n = 1 ~ 7) (type C) is designed and prepared by the hydrosilation of phenylacetylenyl group with dimethylchlorosilane instead of dichloromethylsilane. One 2-benzoxazole-phenyloxy group is substituted on each silicon atom of the dendrimer nG[2,2n-1,1]-22Cl (n = 1 ~ 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[2,2n-1,1]-22BO (n = 1 ~ 7) is purified and isolated quantitatively by silica gel-toluene chromatography. Each dendrimer is characterized by 1H and 13C NMR, MALDI-MS, and elemental analysis. All dendrimers of nG[2,2n-1,1]-22BO (Scheme 3) are soluble in organic solvent such as toluene, diethyl ether, and chloroform. The molecularity of the respective dendrimer nG[2,2n-1,1]-22BO (n = 1 ~ 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[2,2n-1,2]-2n+1PA (n = 1 ~ 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[2,2n-1,2]-28PA, and the last peak from left is that of the lowest generation dendrimer, 1G[2,0,2]-22PA. 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 1st to the 5th generation dendrimers in Figure 1 and 2. On the other hand for the 6th and/or 7th 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 (Mn ≥ Mw). From these results it seems to be reasonable that the closer to 1.00 the PDI value of dendrimer is, the purer dendrimer is obtained. However, in the preparation of the 8th generation 8G[2,2n,2]-22PA no narrow peak in GPC chromatogram is observed.

In conclusion, three types of dendrimer, nG[2,2n-1,2]-2n+1-AN for 9-anthracenemethoxy group substituted dendrimer, nG[2,2n-1,1]-2n-BO for 2-benzoxazole-phenoxy group substituted dendrimer, and nG[2,2n-1,2]-2n+1PA for phenylethynyl group substituted dendrimer, have synthesized up to the 7th 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[2,2n-1,2]-2n+1PA (n = 1 ~ 7) show one λmax at the wavelength of 418 nm (Figure 3). The PL spectra of nG[2,2n-1,2]-2n+1AN (n = 1 ~ 7) show three λmax 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+1PA (n = 1 ~ 7).

Figure 4. Photoluminescent spectra of dendrimers substituted by anthracenemethoxy group nG[2,2^n-1,2]-2^n+1AN (n = 1 ~ 7).

Figure 5. Photoluminescent spectra of dendrimers substituted by 2-benzoxazole-phenoxy group nG[2,2^n+1]-2^nBO (n = 1 ~ 6).

Scheme 4. Suggested mechanism for blue shift of nG[2,2^n+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]-2^nBO (n = 1 ~ 6) show one smaller \( \lambda_{\text{max}} \) at the wavelength of 347 and the other bigger \( \lambda_{\text{max}} \) at the wavelength of 475 nm. Unexpectedly the intensity of the smaller \( \lambda_{\text{max}} \) at the wavelength of 347 nm is increased and the intensity of the bigger \( \lambda_{\text{max}} \) at the wavelength of 475 nm is decreased with increasing the generation of nG[2,2^n+1]-2^nBO, from the 1st to the 6th generation. In the end the intensity of \( \lambda_{\text{max}} \) at the wavelength of 347 nm is bigger than that of \( \lambda_{\text{max}} \) at the wavelength of 475 nm for the 5th and the 6th generation of nG[2,2^n+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-benzoxazolephenoxy group to be planar geometry, in which nitrogen as well as oxygen atoms of the 2-benzoxazole-phenoxy group can coordinate.
equatorially to Si atom. However for the higher generation dendrimer 2-bezoxazole-phenoxy group is too bulky to move around Si atom, therefore the benzoxazole and phenyl groups rotate to minimize their bulkiness (Scheme 4).

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References