

Synthesis of Silafluorene on Dendritic Periphery[†]

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Carbosilane dendrimers with silafluorenyl groups on the periphery were prepared by the reaction of 2,2'-dilithiobiphenyl and dichlorosilyl groups on the carbosilane dendrimers at low temperature. The 1st to 4th generation of dendrimers with silafluorenyl groups were obtained with high yields and the products were purified by column chromatography. The unified properties of the dendrimers were measured by gel permeation chromatography (GPC) and displayed very low and regular polydispersity index (PDI) value. The silafluorenyl moieties on dendritic periphery accepted the potassium fluoride ions which were stabilized by criptand [222], and it proved strong photoluminescent properties.

Key Words : Dendrimer, Silane, Silafluorene, Hydrosilation, Luminescence

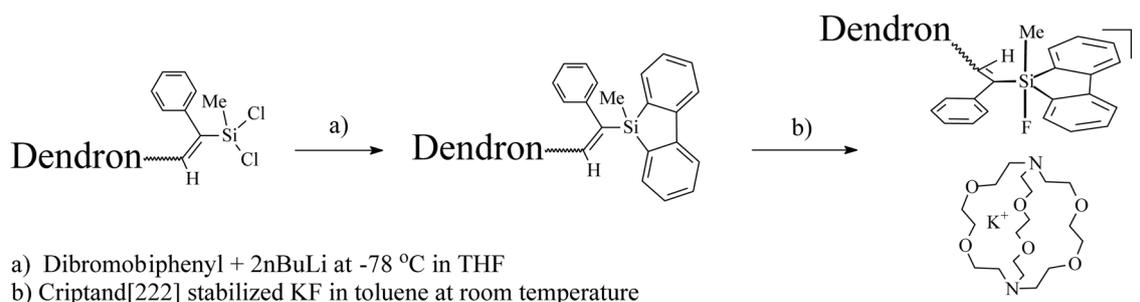
Introduction

Fluorene ring as π -conjugated compound is well known material for the application of important contributions such as luminescence and high electronic acceptability.^{1,2} Theoretical calculation regarding HOMO-LUMO energy level and conventional synthetic approach of the functionalized ring has also been demonstrate.^{3,4} Although the formation of silicon contained fluorenes was even observed under the different condition, the synthetic methods and applications of its dendritic properties are rarely appeared on papers. The π -conjugated molecules containing silicon atom possess unique electronic properties owing to their low lying LUMO associated with σ^* and π^* conjugation.⁴ The silafluorenyl function on dendritic periphery as a unique number is, therefore, highly desired to develop a new area for the synthesis and application of silafluorenes based dendrimers. The change of the coordination number of the main group element represents a new strategy for the control of their electronic properties.⁵ Addition of small polar anions to tetra-coordinated silane is attracted and growing attention because of its great potential for luminescent applications.⁶ The photoluminescence properties of penta-coordinated silane were given strongly different properties from their tetra-coordinated silicon compounds.⁷ We, recently have

prepared the carbosilane dendrimers with triple bonds at the periphery.⁸ These products exhibited the photoluminescent properties with very low intensity. We have incorporated silafluorene functions onto the carbosilane dendrimers by cross-coupling methods so far.⁴ The addition of well-defined chemicals onto the dendritic core as well as the periphery with predetermined synthetic methods is used and it is also very useful application for dendritic researches. The preparative methods of silafluorene is a well known chemical process through the reaction of lithiated biphenyl and dichlorosilane at low temperature. Naturally, the preparation of 5-coordinated silanes was also a known process by the use of an activated anion such as fluoride. Lately, preparative methods of carbosilane and the silafluorene as well as 5-coordination properties of silanes were independently developed. From this topological viewpoint, we tried to incorporate silafluorenyl groups to the carbosilane dendrimer and continually studied the 5-coordination properties of the dendritic branches.

Results and Discussion

The dendrimers with silafluorene on the dendritic periphery were prepared by direct cross-coupling between a carbosilane dendron with the terminal dichlorosilylmethyl



Scheme 1. Preparative way of the silafluorene dendrimer and 5-coordinated silafluorene dendrimer.

[†]This paper is dedicated to Professor Sang Chul Shim on the occasion of his honorable retirement.

moiety and lithiated biphenyl at low temperature. It was progressed by the reaction of 2,2'-dibromobiphenyl and butyllithium (2 equivalent) at $-78\text{ }^{\circ}\text{C}$ and followed by continual addition of carbosilane dendron with dichlorosilyl end-functions (Gn-mCl) into the lithiated biphenyl. The inner shells of the carbosilane dendrimers were prepared via bis(phenylethynyl)dimethylsilane as core. The next generation was obtained by the use of hydrosilation between dichloromethylsilane and two triple bonds on each dendritic branch.⁸ The triple bonds on dendritic periphery were obtained by the substitution of lithiumphenylacetylide to dichloromethylsilyl groups. The products were obtained in yields greater than 95%, and were confirmed through ^1H NMR spectroscopy. The inner shell dendrimers based on only ethylsilane were purified by column chromatography over silica gel using toluene as an eluent. The unified properties of the dendrimers were obtained by GPC methods which provided very narrow PDI value and regular signal

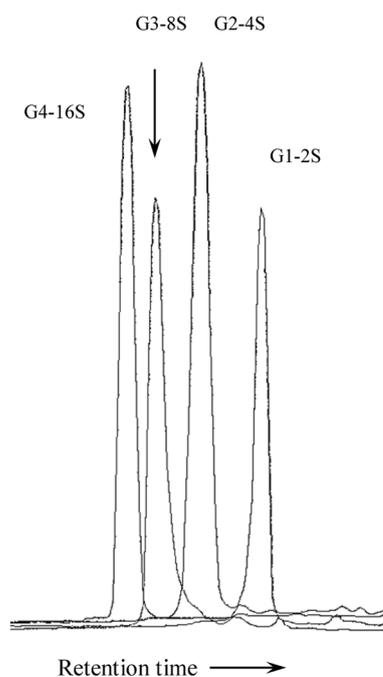
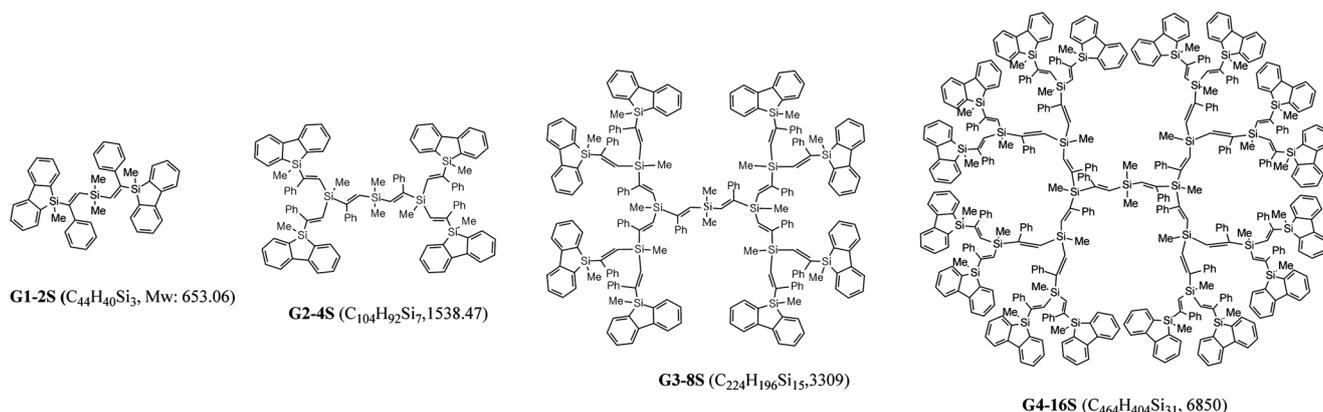


Figure 1. GPC diagram of silafluorene dendrimers.



Scheme 2. Planner view of silafluorene 1st to 4th generation dendrimers.

position (Fig. 1).

The silafluorenyl dendrimers (Gn-mS) were prepared by the reaction between the dichlorosilyl branches on ethynylsilane dendrimers and lithiated 2,2'-dibromobiphenyl at low temperature. The lithium salt and excess reactants were removed by column chromatography. The silafluorene dendrimers were obtained with high yields. The characteristic silafluorene groups were identified by NMR. The methyl groups on silafluorene moiety were observed at 0.38 ppm for G1-2S, 0.31 ppm for G2-4S, 0.27 ppm for G3-8S, and 0.25 ppm for G4-16S, which were viewed as singlets, and other silafluorenyl dendrimers were observed with the same pattern.

The measurements of MALDI-TOF mass spectroscopy provided the molecular information of silafluorenyl dendrimers providing 1562 Dalton for G2-4S and 3336 Dalton for G3-8S indicating that $\text{M} + \text{Na}$ ion was detected in the condition, but G4-16S dendrimer was not in progress in molecular ion peaks and fragmentation peaks. The purity and unified properties of silafluorenyl dendrimers were observed by GPC. The chromatograms of dendrimers showed one narrow signal with low PDI value indicating that the prepared dendrimers were pure and didn't contain any other byproduct. The retention time of dendrimers was regularly decreased by increasing generations. Specially, single signal at 20.61 min with PDI value of 1.09, at 18.96 min with PDI value 1.01, at 16.95 min with PDI at 1.01, and at 16.95 min 1.00 for the first (G1-2S), second (G2-4S), third (G3-8S) and fourth (G4-16S) respectively (Figure 1). The products were obtained after column chromatography as light yellow powders, and the yields were 65-70%.

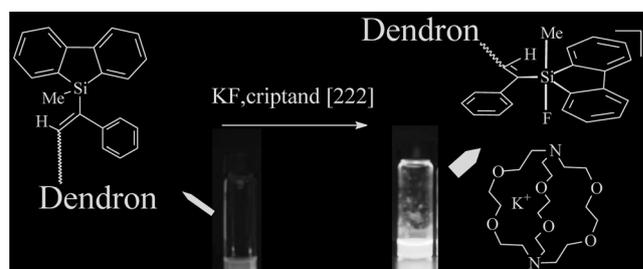


Figure 2. Photographs of photoluminescent of 4-coordinated [left] and 5-coordinated silafluorene [right] dendrimer.

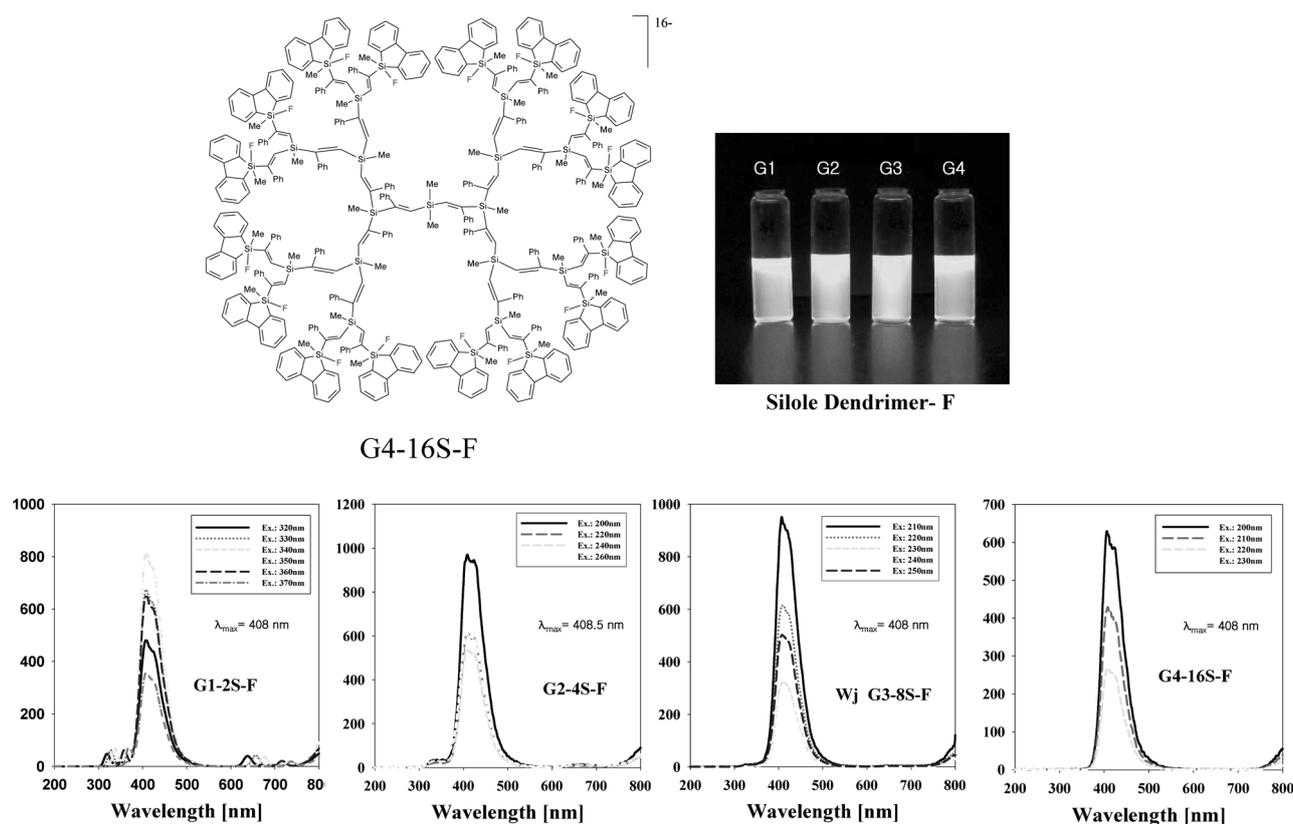


Figure 3. Planar view of 5-coordinated 4th generation of silfluorenyl dendrimer (G4-16S-F), Photographs of photoluminescent of 5-coordinated silfluorene dendrimers, and PL spectra of Gn-mS-F type dendrimers (G1-2S-F to G4-16S-F).

Experimental

The silfluorene dendrimers were produced with low photoluminescent value. Accordingly, the penta-coordinated dendrimer was prepared by continual work. It was prepared by the addition of equimolar amounts of KF and criptand [222] to toluene solution of silfluorene dendrimers at room temperature. The coordination of fluoride ions to the silicone atom was detected by NMR spectroscopy. The addition of criptand stabilized KF to dendritic solution markedly increasing the photoluminescent properties. All of the silfluorene dendrimers were prepared under the dried nitrogen atmosphere.

The preparation and purification of G1-2S. 3.84 mmol of *n*-butyllithium was slowly added to 50 mL of cold THF solution (−78 °C) of 0.56 g (1.78 mmol) of 2,2-dibromobiphenyl and stirred at this temperature for 1 h. And 0.39 g (0.80 mmol dissolved in 25 mL THF) of the first generation G1-4Cl was continually added to the cold solution and stirred at room temperature for 12 h. The lithium salt and excess reactants were removed by column chromatography with silicagel and eluted with mixture of THF and hexane. Yield: 0.34 g (0.52 mmol, 65.00%) as colorless solid. ¹H NMR (ppm, CDCl₃): δ = −0.55 (s, 6H, SiMe, G0), 0.38 (s, 6H, SiMe, G1), 6.33 (s, 2H, CH=C, G0), 6.77–6.87, 7.00–7.13, 7.13–7.30, 7.35–7.55, 7.55–7.90 (m, 26H, Silfluorene). ¹³C NMR (ppm, CDCl₃): δ = −4.81 (SiMe, G0), −0.59

(SiMe, G1), 120.86, 126.02, 127.26, 127.55, 130.18, 133.44, 137.00, 144.02, 147.80, 147.93 (silfluorene and Ph), 148.13, 159.54 (CH=C, G0). GPC: PDI (Mw/Mn) = 1.095 (246/225); Rt, 20.61 min. Anal. calcd. for C₄₄H₄₀Si₃ (Mw = 653.14): C, 80.92%, H, 6.17%. Found: C, 80.25%, H, 5.92%. UV/Vis: λ_{max} = 278 nm, ε_{max} = 0.10 × 10⁵.

The preparation and purification of G2-4S. It was used the same methods as the preparation of G1-2S. The reaction was carried out by using 0.44 g (1.41 mmol) of 2,2-dibromobiphenyl in 50 mL THF, 3.04 mmol of *n*-butyllithium, and 0.39 g (0.32 mmol) of G2-8Cl. Yield: 0.32 g (0.21 mmol, 65.63%) as a colorless solid. ¹H NMR (ppm, CDCl₃): δ = −0.83 (s, 6H, SiMe, G0), −0.59 (s, 6H, SiMe, G1), 0.31 (s, 12H, SiMe, G2), 5.85 (s, 2H, CH=C, G0), 6.25 (s, 4H, CH=C, G1), 6.50–6.70, 6.85–7.07, 7.10–7.25, 7.25–7.50, 7.70–7.85 (m, 62H, silfluorene). ¹³C-NMR (ppm, CDCl₃): δ = −4.71 (SiMe, G0), −2.81 (SiMe, G2), −0.60 (SiMe, G1), 120.81, 125.66, 125.99, 127.23, 127.41, 130.14, 133.42, 136.87, 137.01, 143.70, 144.95, 145.09, 145.27, 145.44 (silfluorene and Ph), 148.08, 162.93 (CH=C, G0), 148.11, 160.13 (CH=C, G1). GPC: PDI (Mw/Mn) = 1.011 (1,535/1,519); Rt, 18.96 min. Anal. calcd. for C₁₀₄H₉₂Si₇ (Mw=1538.66): C, 81.19%, H, 6.03%. Found: C, 80.97%, H, 5.64%. UV/Vis: λ_{max} = 279 nm, ε_{max} = 0.25 × 10⁵.

The preparation and purification of G3-8S. It was used the same methods as the preparation of G1-2S. The reaction was carried out by using 0.40 g (1.27 mmol) of 2,2-dibromo-

biphenyl in 25 mL THF, 2.27 mmol of *n*-buthyllithium 0.37 g (0.14 mmol) of G3-16Cl. Yield: 0.33 g (0.10 mmol, 71.43%) as a colorless solid. ¹H NMR (ppm, CDCl₃): δ = -0.90 (s, 12H, SiMe, G2), -0.84 (s, 6H, SiMe, G0), -0.50 (s, 6H, SiMe, G1), 0.27 (s, 24H, SiMe, G3), 5.86 (s, 4H, CH=C, G1), 5.92 (s, 2H, CH=C, G0), 6.17 (s, 8H, CH=C, G2), 6.48-6.63, 6.63-6.70, 6.80-7.10, 7.10-7.20, 7.20-7.50, 7.70-7.85 (m, 134H, silafluorene). ¹³C-NMR (ppm, CDCl₃): δ = -4.75 (SiMe, G2), -2.95, SiMe, G3), -2.63 (SiMe, G0), -0.07 (SiMe, G1), 120.80, 125.75, 125.96, 127.24, 127.39, 127.92, 129.13, 130.14, 133.43, 136.85, 137.01, 142.25, 142.43, 143.62, 144.58, 144.75, 145.19, 148.07 (silafluorene and Ph), 159.83, 164.25 (CH=C, G0-G1), 160.04, 163.87 (CH=C, G2). GPC: PDI (Mw/Mn), 1.005 (2,267/2,255); Rt, 17.78 min. Anal. calcd. for C₂₂₄H₁₉₆Si₁₅ (Mw = 3309.70): C, 81.30%, H, 5.97%. Found: C, 81.02%, H, 4.92%. UV/Vis: λ_{max} = 279 nm, ε_{max} = 0.77 × 10⁵.

The preparation and purification of G4-16S. It was used the same methods as preparation of G1-2S. The reaction was carried out by using 0.84 g (2.69 mmol) of 2,2-dibromobiphenyl in 25 mL of THF, 5.92 mmol of *n*-buthyllithium and 0.58 g (0.15 mmol) of G4-32Cl. Yield: 0.50 g (0.096 mmol, 64.00%) as colorless solid. ¹H NMR (ppm, CDCl₃): δ = -0.90 (s, 36H, SiMe, G2-G3), -0.70 (s, 6H, SiMe, G0), -0.55 (s, 6H, SiMe, G1), 0.25 (s, 48H, SiMe, G4), 5.78 (s, 4H, CH=C, G1), 5.85 (s, 2H, CH=C, G0), 6.15 (s, 24H, CH=C, G2-G3), 6.40-6.60, 6.60-6.70, 6.75-7.05, 7.05-7.20, 7.20-7.50, 7.65-7.85 (m, 278H, silafluorene). ¹³C NMR (ppm, CDCl₃): δ = -4.71 (SiMe, G2-G3), -2.92 (SiMe, G4), -2.29, SiMe, G0), 0.07 (SiMe, G1), 120.78, 125.96, 127.25, 127.39, 129.24, 130.15, 133.43, 136.76, 136.85, 136.92, 137.01, 141.85, 143.57, 144.59, 144.82, 145.19, 148.06 (silafluorene and Ph), 159.71, 164.94 (CH=C, G0-G2), 159.98, 163.90 (CH=C, G3). GPC: PDI (Mw/Mn), 1.001 (2,733/2,730); Rt, 16.95 min. Anal. calcd. for C₄₆₄H₄₀₄Si₃₁ (Mw = 6851.78): C, 81.35%, H, 5.94%. Found: C, 80.82%, H, 5.63%. UV/Vis: λ_{max} = 279 nm, ε_{max} = 2.27 × 10⁵.

A typical procedure for the preparation of 5-coordinated silafluorene dendrimers (Gn-mS-F).

Preparation of G1-2S-F: The mixture of dendrimer G1-2S (30 mg, 0.046 mmol), 35 mg (0.093 mmol) of criptand [222], and 5.9 mg (1.01 mmol) of anhydrous KF were stirred to form yellow precipitate at room temperature for two days. Toluene was removed by reducing pressure and the precipitate was washed with pentane (10 mL × 2). Yellow

solids were isolated. The G2-4S-F, G3-8S-F, and G4-16S-F were prepared by the same method. ¹⁹F NMR (in pyridine *d*⁵) of G1-2S-F showed 1 single signal at -124.49 ppm.

Measurement of photoluminescence: Perkin-Elmer luminescence spectrometer LS45 (Xenon flash tube) was used for the measurement of the spectrum. The 1st to 4th generation of 5-coordinated silafluorene carbosilane dendrimer showed blue emission maxima at 407.5-408.5 nm. All 5-coordinated silafluorene dendrimers showed stronger blue photoluminescence but 4-coordinated dendrimers were showed no PL spectra (Fig. 2 and 3). It was also found that PL intensity was improved according to the increase of generations.

In summary, silafluorene dendrimers were prepared by the reaction of lithiated biphenyl and chlorinated dendrimers containing Gn-2mCl groups on periphery. The penta-coordinated silafluorene dendrimers were prepared by the addition of criptand [222] and KF to the dendrimer which showed strong photoluminescent properties.

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