

Preparation and Diels–Alder reaction of carbosilane dendrimer with conjugated diene

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Abstract

The carbosilane dendrimers with 12, 36, 108 and 324 diene groups on the periphery have been prepared. The first generation with 12 diene groups which react with enes such as *N*-ethylmaleimide, 1,4-naphthoquinone, and tetracyanoethene has produced the Diels–Alder products (DA) on the dendritic periphery. The NMR and MALDI-TOF mass spectra have characterized the DA products. The unified dendritic character has been observed by gel permeation chromatography.

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Keywords: Dendrimers; Diels–Alder polymers; Polysilanes; MALDI; Hexadiene

1. Introduction

Dendrimers with highly branched structures have appeared as a new range of materials [1–4]. Carbosilane dendrimers were prepared by simple growth methods such as hydrosilation which is well known procedure for the purpose of increasing branches on carbosilane dendrimers [5–9]. And continually the addition of functional groups onto the dendritic periphery has been established by the reaction between chlorosilyl groups and methalorganyls such as lithium-organyl as well as Grignard reagent [10,11]. Mono-functional groups on the carbosilane dendritic branch such as allyl or allyloxy groups can progress to the next generation with maximum three times more new branches by hydrosilation with chlorosilane [12]. And the other side, bi- and more functional groups such as diene on a dendritic branch can be progressed to the new generation with maximum six and more

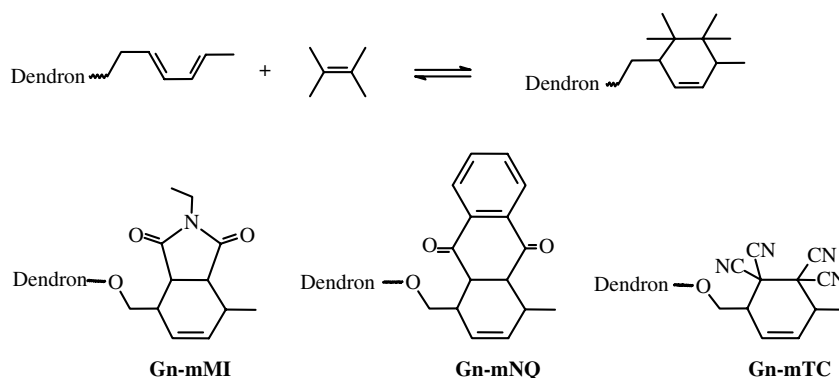
new branches [13]. But until now, the information about the hydrosilation process of two or more double bonds in one branch has been so far that cannot clearly progress to the next generation with regioselective properties. Therefore, this paper deals with only the Diels–Alder reaction of conjugated diene branches on the dendritic periphery (Scheme 1).

2. Results and discussion

The dendrimer with conjugated 2,4-hexadienyl-1-oxy branches on the periphery can be prepared by the use of the same manner as our previous works [12]. The addition of conjugated diene-branches on carbosilane dendrimers has started with the hydrosilation of vinyl groups on the core molecule with the excess of trichlorosilane. The first parent generation with 12 chlorosilyl groups (G1-12Cl) has converted into the 12-hexadienyl groups containing the dendrimer G1-12HD by the reaction of 2,4-hexadien-1-ol at RT in the toluene medium. The second generation including the conjugated 36-dienyl groups on the periphery (G2-36HD) has been

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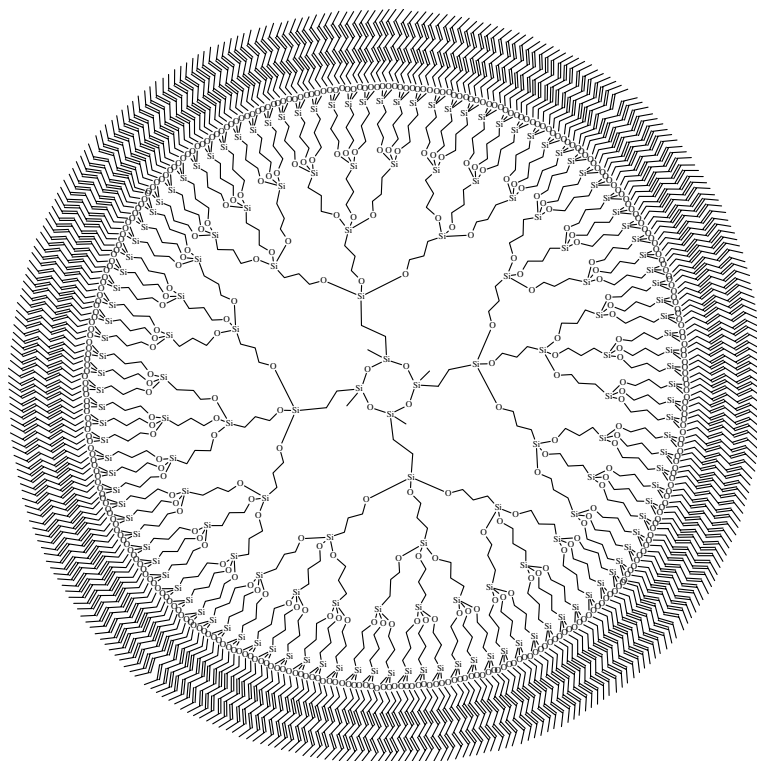


Scheme 1. Schematic view of dendritic peripheral functions by Diels–Alder reaction.

prepared by the use of parent dendrimer G2-36Cl and the conjugated dienol which prepares the inner shell by the addition of allyl groups before the addition of peripheral hexadienyl functions. Repeating these methods has prepared G3-108HD and G4-324HD. Each of two steps such as hydrosilation of allyl groups with trichlorosilane and the addition of 2,4-hexadien-1-ol group procedure has provided almost quantitative yields (Scheme 2).

The pure hexadienyl dendrimer Gn-mHD has been obtained by simple chromatography using silica gel-toluene combination. The excess of 2,4-hexadien-1-ol, TME-DA and solvated salts were removed by this method. The small amounts of unknown products as well as polymerized products which might be formed by moisture during

handling process have been also removed by the method. The first to the fourth generations have yielded colorless wax like liquid whose fluid decreased according to the increasing generation. All generations were soluble in a wide range of solvents including hydrocarbon. Yield was very high and existed as clear gel type. The ^1H NMR spectra of the Gn-mHD dendrimers have provided a unique property through the first to the fourth generations, which can be easily detected by characteristic signals at 5.0–5.2 and 5.3–5.4 ppm for double bonds, and 4.1–4.4 ppm for $-\text{OCH}_2-$ groups for each generation of peripheral functions. In addition, the elemental analysis has shown very near values for the calculated one. The unimolecular properties of prepared dendrimers have been determined by GPC measurements (Fig. 1). The



Scheme 2. Planar view of G4-324 HD with molecular weight 45,304 Dalton and 324 dienyl groups.

chromatograms of dendrimers have shown one signal with low polydispersity index value (PDI). If the dendrimers have impurities in the product, the GPC diagram will detect small signal or shoulder on the left side of the main signal because the impurity is caused by unreacted chlorosilyl groups. The hydrolysis of unreacted chlorosilyl groups on dendrimers has formed the dimmer or higher polymer type dendrimers through the elimination of hydrogen chloride by atmospheric moisture. The retention time of dendrimers were decreased with increasing generation, which means that the prepared dendrimers are pure and contain no other chemical process. Practically, the chromatogram has one single signal at 18.05 min with PDI value 1.007 for the first generation (G1-12HD), 16.81 min and 1.002 for the second generation (G2-36HD), 16.18 min and 1.009 for the third generation (G3-108HD), and 15.35 min, and 1.190 for the fourth generation. The GPC data have produced very regular property about retention time and the polydispersity value. MALDI TOF mass spectrum of G1-12HD dendrimer has shown one signal of $[M + Na]^+$

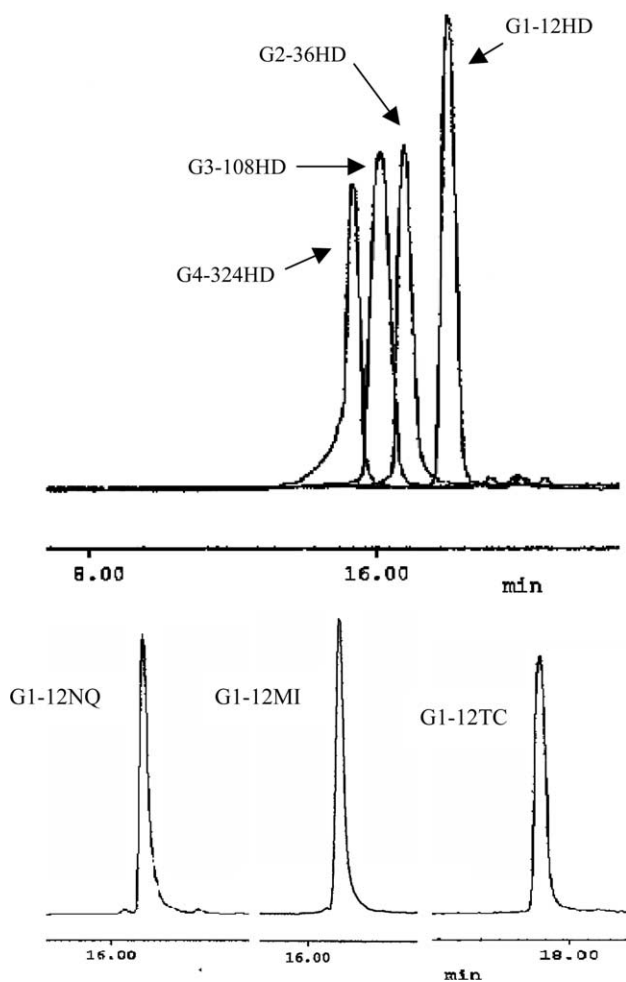


Fig. 1. GPC chromatogram of G1-HD–G4-HD (up) and Diels–Alder Products of G1-12NQ, G1-12MI, G1-12TC (down).

ion at 1648 amu (Fig. 2). Higher generations have not provided any molecular ion peak.

The Diels–Alder reaction of conjugated dienyl groups on dendrimer Gn-mHD with *N*-ethylmaleimide (MI), 1,4-naphthoquinone (NQ) and tetracyanoethene (TC) has been performed under the refluxed condition in toluene for the preparation of G1-12MI and G1-12NQ and at the room temperature condition for the preparation of G1-12TC dendrimer (Scheme 3). In all these cases, reactions have been monitored by ^1H NMR, which includes total disappearance of conjugated dienyl groups on G1-12HD dendrimer and forms new signals at the bicyclo area (3.00–5.00 ppm) on the Diels–Alder products. The DA products have been identified by characteristic hyperfine ^1H NMR spectrum between chemical shifts 3.00–5.00 ppm (Figs. 3 and 4). We tried to prepare simple standard DA products from the reaction of 2,4-hexadien-1-ol, and ethylmaleimide, as well as 1,4-naphthoquinone. The standard DA product has been performed by the use of hyperfine NMR spectrum (600 MHz), which can be easily detected by the characteristic signals from 3.0 to 5.0 ppm. By the high-resolution ^1H NMR, the G1-12MI, G1-12NQ and G1-12TC dendrimers were determined same result such as simple DA products. The selected ^1H NMR data and coupling constants for the DA products are given in Figs. 3 and 4. The hyperfine ^1H NMR spectrum of the DA product G1-12MI has observed interesting structural information at 3.34 ppm for H_3 , 2.58 ppm for H_4 , 2.44 ppm for H_7 , and 3.04 ppm for H_8 respectively, and the coupling constant J_{3-4} and J_{7-8} have revealed 7.80 Hz (Fig. 3). This result has been followed by the Karplus curve that has coupling at the vicinal inter-proton between H_3 and H_4 as well as H_7 and H_8 . According to this, the dihedral angle between $\text{H}_3\text{--C}_3\text{--C}_4\text{--H}_4$ and $\text{H}_7\text{--C}_7\text{--C}_8\text{--H}_8$ is about 170° . The dihedral angles $\text{H}_4\text{--C}_4\text{--C}_5\text{--H}_5$ and $\text{H}_6\text{--C}_6\text{--C}_7\text{--H}_7$ of about 100° with coupling constant $^3J_{\text{H}_4\text{--H}_5}$ and $^3J_{\text{H}_6\text{--H}_7}$ are 1.30 Hz. This verifies the Karplus prediction of the configuration. Therefore, the Diels–Alder reaction has progressed under the same pattern and the product has been obtained by the cisoid arrangement of reactants. The other dendrimers G1-12NQ and G1-12TC have been shown in the same manner as the previous product (Figs. 3 and 4).

The MALDI-mass spectra of G1-12MI have mainly shown one molecular ion peak at 3146 amu that is clearly due to the first generation with 12 of DA products and one sodium ion on the carbosilane dendrimer. The dendrimers G1-12NQ and G1-12TC have been shown in principle M^+ peak. The second generation dendrimers G2-36DI, G2-36NQ and G2-36TC and higher generation dendrimers have not shown any molecular ion peak. The unimolecular properties of DA products of first generations (G1-12NQ, G1-12TC and G1-12MI) have been determined by GPC measurements. The chromatograms of the first generation of DA products have shown one

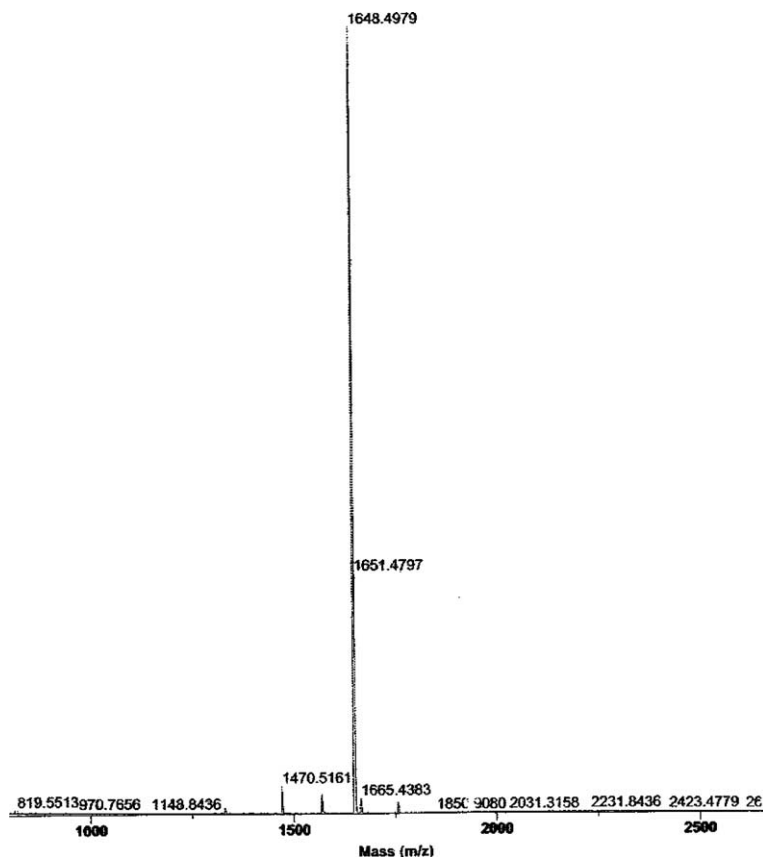


Fig. 2. MALDI mass spectrum of G1-12HD.

signal with narrow polydispersity index value but, the second generation dendrimers showed single narrow signal. The second and the third generation of dendrimers have shown the impure GPC diagram that detects small signal or shoulder by the left side of the main signal according to the impurity.

The result of MALDI-TOF mass and GPC chromatography have showed that the DA reactions of higher generations have not produced unified molecular dendrimers. This result proposes that the dendritic surfaces of the second and the third generation are smaller than the summation of additional groups.

To summarize, we have demonstrated the versatile synthesis of multi-functional dendrimers that enable a new synthetic approach. These conjugated branches can be potentially used for the family of Diels–Alder reactions on dendritic periphery. Further works on the reaction of conjugated double bonds have been aimed in the progress (Scheme 3).

3. Experimental section

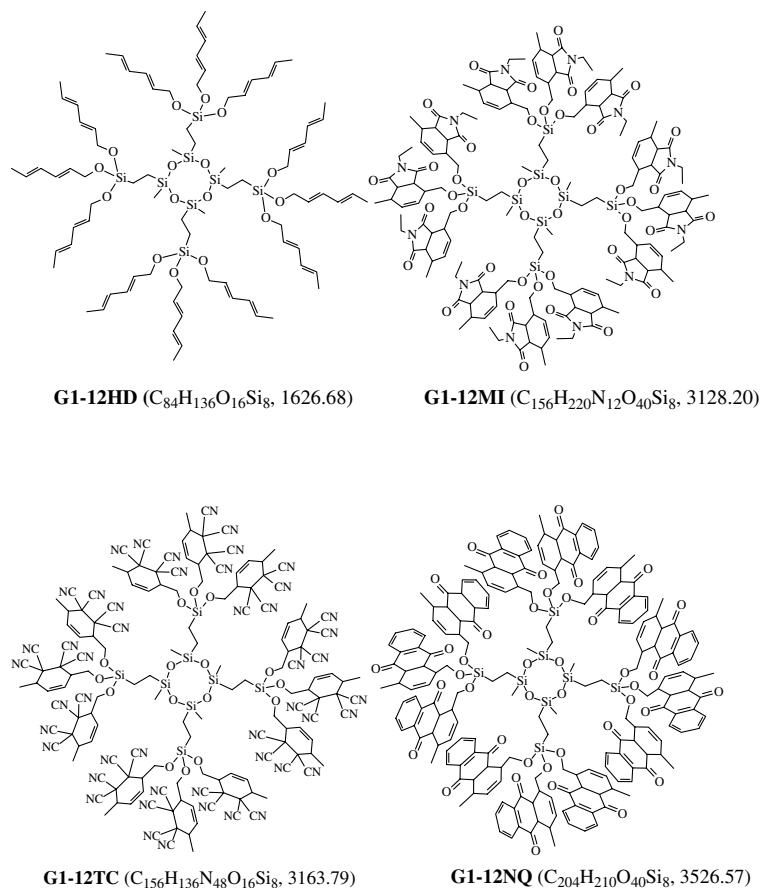
3.1. General

All reactions have been performed under dried N_2 atmosphere. The NMR spectra were recorded on a

Bruker AC-200 Spectrometer. GPC has been performed in THF at 25 °C with Waters 515 HPLC pump together with Waters 2410 Refractive Index detector. For the GPC, three 7.8×30 cm columns (Ultrastayragel, 7.8×30 cm; 10^3 , 10^4 , 10^5) have been connected in series and calibrated with the narrow molecular weight polystyrene standard. The Busan and Daejon Branches of the Korean Basic Science Institute (KBSI) have performed high resolution NMR spectrum (Bruker, DMX-600), MALDI mass (Voager DE-STR 4700 Proteomics Analyzer) and elemental analysis (Vario EL).

3.2. *Gn-mHD*

For the preparation of G1-12HD: The mixture of 2.22 g (21.41 mmol) of well-dried 2,4-hexadienyl-1-ol by molecular sieve and 2.48 g (21.34 mmol) of TME-DA in 25 ml of toluene were slowly added to 1.31 g of G1-12Cl (1.49 mmol: first generation with four times of trichlorosilyl groups) in 50 ml toluene. The mixture was warmed about 60 °C for 30 min, cooled in room temperature and filtered with the reaction mixture. The solvent was removed from the filtrate. The residue has been progressed the flash chromatography with silica gel–toluene. Yield 2.05 g (1.26 mmol,



Scheme 3. Planar view of G1-12HD, G1-12MI, G1-12TC and G1-12NQ.

85%) of clear colorless liquid. The same method as this of G1-12HDI has been used for the preparation of higher generations G2-36HD, G3-108HD and G4-324HD.

3.3. G1-12HD

Yield: 2.05 g (1.26 mmol, 85%) as colorless difficult fluid liquid. ¹H NMR (ppm, CDCl₃): δ = 0.05 (s, 12H,

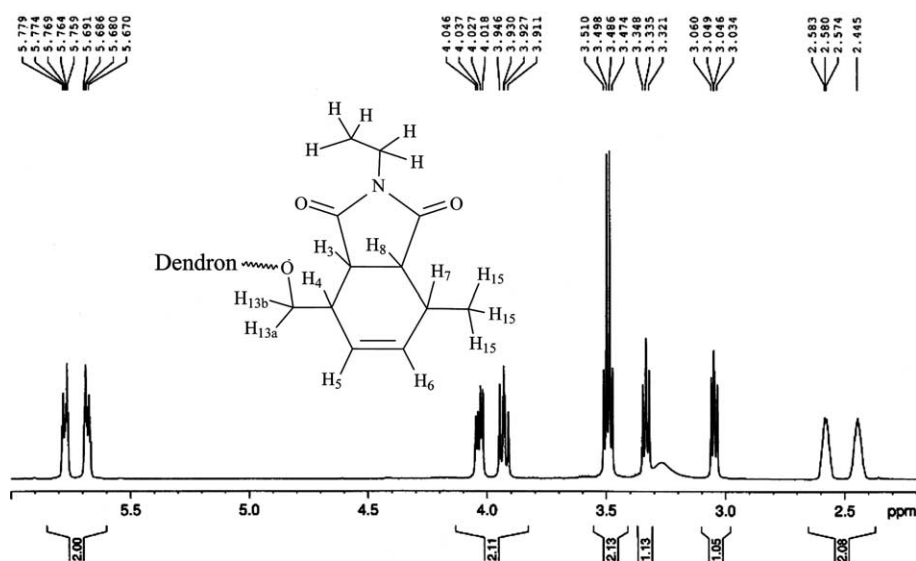


Fig. 3. ¹H NMR spectrum and coupling constant of DA product G1-12MI. Chem. Shift (ppm): H3, 3.3453; H4, 2.580; H5, 5.764; H6, 5.686; H7, 2.445; H8, 3.047; H10, 3.492; H13a, 3.930; H13b, 4.032; H14, 3.270. Coupling constant (Hz): ³J(3–4), 7.80; ³J(3–8), 8.10; ³J(4–5), 1.30; ⁴J(4–6), 1.80; ³J(4–13a), 9.60; ³J(4–13b), 5.40; ³J(5–6), 9.80; ⁴J(5–7), 1.80; ³J(6–7), 1.30; ³J(7–8), 7.80; ³J(7–15), 6.37; ⁴J(13a–13b), 11.40.

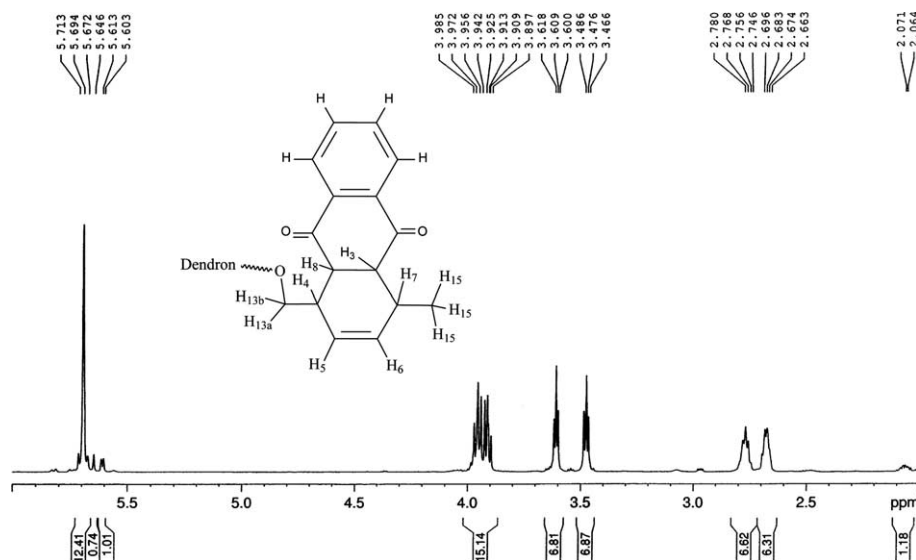


Fig. 4. ^1H NMR spectrum and coupling constant of DA product G1-12NQ. Chemical shift (ppm): H8, 3.609; H4, 2.762; H5, 5.962; H6, 5.964; H7, 2.679; H3, 3.476; H13a, 3.911; H13b, 3.964; H15, 0.80. Coupling constant (Hz): $^3J(3-4)$, 5.40; $^3J(3-8)$, 6.00; $^3J(4-5)$, 5.00; $^4J(4-6)$, 1.80; $^3J(4-13a)$, 7.00; $^3J(4-13b)$, 8.00; $^3J(5-6)$, 9.80; $^4J(5-7)$, 1.80; $^3J(6-7)$, 1.30; $^3J(7-8)$, 6.00; $^3J(7-15)$, 6.37; $^4J(13a-13b)$, 11.40.

SiMe (G0), 0.45–0.76 (m, 16H, SiCH₂ (G0)), 1.62–1.93 (m, 36H, CH₃ (G1)), 4.18–4.45 (m, 24H, OCH₂ (G1)), 5.54–5.80, 5.93–6.32 (m, 48H, =CH (G1)). ^{13}C NMR (ppm, CDCl₃): δ = -1.48 (SiMe (G0)), 1.76, 7.94 (SiCH₂ (G0)), 18.09 (CH₃ (G1)), 63.28 (OCH₂ (G1)), 128.93, 129.20, 129.43 (=CH (G1)). Anal. calc. for C₈₄H₁₃₆O₁₆Si₈ (M_w : 1624): C, 62.07; H, 8.37. Found: C, 61.98; H, 8.30%. GPC: PDI (M_w/M_n) = 1.007 (1887/1873), R_t = 18.05 min.

3.4. G2-36HD

For the preparation of G2-36HD, 2.82 g (28.73 mmol) of well-dried 2,4-hexadienyl-1-ol, 3.85 g (33.12 mmol) of TMEDA, 1.75 g of G2-36Cl (0.63 mmol) and 50 ml toluene as solvent have used. Yield: 2.54 g (0.51 mmol, 80%) as colorless difficult fluid liquid. ^1H NMR (ppm, CDCl₃): δ = 0.07 (s, 12H, SiMe (G0)), 0.44–0.78 (m, 16H, SiCH₂ (G0)), 1.43–1.89 (m, 156H, CH₂ (G1), CH₃ (G2)), 3.58–3.78 (m, 24H, OCH₂ (G1)), 4.21–4.42 (m, 72H, OCH₂ (G2)), 5.52–5.78, 5.93–6.33 (m, 144H, =CH (G2)). ^{13}C NMR (ppm, CDCl₃): δ = -1.50 (SiMe (G0)), 1.46, 7.82 (SiCH₂ (G0)), 6.31, 25.71 (CH₂ (G1)), 18.06 (CH₃ (G2)), 63.18 (OCH₂ (G2)), 64.96 (OCH₂ (G1)), 128.83, 129.28, 130.95 (=CH (G2)). Anal. calc. for C₂₆₄H₄₂₄O₅₂Si₂₀ (M_w : 4984): C, 63.56; H, 8.51. Found: C, 63.25; H, 8.48%. GPC: PDI (M_w/M_n) = 1.002 (2804/2798), R_t = 16.81 min.

3.5. G3-108HD

For the preparation of G3-108HD, 2.62 g (26.71 mmol) of well-dried 2,4-hexadienyl-1-ol, 3.08 g (26.50

mmol) of TMEDA, 1.72 g of G3-108Cl (0.20 mmol) and 50 ml toluene have been used. Yield: 2.35 g (0.16 mmol, 76%) as colorless difficult fluid liquid. ^1H NMR (ppm, CDCl₃): δ = 0.07 (s, 12H, SiMe (G0)), 0.45–0.80 (m, 64H, SiCH₂ (G0), CH₂ (G1)), 1.45–1.93 (m, 468H, CH₂ (G2), CH₃ (G3)), 3.53–3.80 (m, 96H, OCH₂ (G1, G2)), 4.19–4.43 (m, 216H, OCH₂ (G3)), 5.48–5.83, 5.93–6.33 (m, 432H, =CH (G3)). ^{13}C NMR (ppm, CDCl₃): δ = -1.48 (SiMe (G0)), 1.46, 7.82 (SiCH₂ (G0)), 6.31, 25.71 (CH₂ (G1)), 8.97, 25.65 (CH₂ (G2)), 18.01 (CH₃ (G3)), 63.09 (OCH₂ (G3)), 64.81, 65.07 (OCH₂ (G1, G2)), 128.80, 129.13, 130.88 (=CH (G3)). Anal. calc. for C₈₀₄H₁₂₈₈O₁₆₀Si₅₆ (M_w : 15,064): C, 64.05; H, 8.55. Found: C, 63.89; H, 8.53%. GPC: PDI (M_w/M_n) = 1.009 (3538/3503), R_t = 16.18 min.

3.6. G4-324HD

For the preparation of G4-324HD, 3.04 g (30.99 mmol) of well-dried 2,4-hexadienyl-1-ol, 3.85 g (33.12 mmol) of TMEDA, 2.03 g of G4-324Cl (0.08 mmol) and 50 ml toluene have been used. Yield: 2.92 g (0.06 mmol, 81%) as colorless difficult fluid liquid. ^1H NMR (ppm, CDCl₃): δ = 0.07 (s, 12H, SiMe (G0)), 0.40–0.75 (m, 208H, SiCH₂ (G0), CH₂ (G1, G2)), 1.43–1.88 (m, 1404H, CH₂ (G3), CH₃ (G4)), 3.48–3.78 (m, 312H, OCH₂ (G1, G2, G3)), 4.15–4.39 (m, 648H, OCH₂ (G4)), 5.48–5.78, 5.85–6.30 (m, 1296H, =CH (G4)). ^{13}C NMR (ppm, CDCl₃): δ = -1.48 (SiMe (G0)), 1.46, 7.82 (SiCH₂ (G0)), 6.31, 25.71 (CH₂ (G1)), 8.97, 25.65 (CH₂ (G2)), 6.32, 25.79 (CH₂ (G3)), 18.10 (CH₃ (G4)), 63.13 (OCH₂ (G4)), 64.88, 65.14 (OCH₂ (G1, G2, G3)), 128.99, 130.86, 131.04 (=CH (G4)).

Anal. calc. for $C_{2424}H_{3880}O_{484}Si_{164}$ (45,304): C, 64.21; H, 8.56. Found: C, 63.37; H, 8.48%. GPC: PDI (M_w/M_n) = 1.190 (8084/6738), R_t = 15.35 min.

3.7. Preparation of G1-12MI

0.51 g (0.33 mmol) of G1-12HD and 1.00 g (7.83 mmol) of *N*-ethylmaleimide were dissolved in 25 ml of toluene and refluxed for 3 h. The volatile components were removed under vacuum, leaving yellow precipitate. By the 1H NMR spectrum of reaction mixture, all the hexadiene signals in G1-12HD have been converted into the new orientation, and the bicyclo signals have been observed in the new area from 4.60 to 4.82 ppm. The solvent was removed under vacuum. The *N*-ethylmaleimide free-product has been obtained by washing the reaction mixture with pentane. Yield: 0.81 g (0.26 mmol, 82%) of light yellow powder. The same method as that of G1-12MI has been used for the preparation of G1-12NQ and G1-12TC. Yield: 0.27 g (0.086 mmol, 82%) as light yellow waxy type solid. 1H NMR (ppm, $CDCl_3$): δ = 0.10 (s, 12H, SiMe (G0)), 0.52–0.81 (m, 16H, SiCH₂ (G0)), 0.95–1.22 (m, 36H, CH₃ (MI)), 1.35–1.58 (m, 36H, CH₃ (G1)), 2.32–2.65 (m, 24H, CH (G1)), 2.94–3.10, 3.18–3.30 (m, 24H, CH (G1)), 3.30–3.62 (m, 24H, CH₂ (MI)), 4.10–4.28, 4.33–4.50 (m, 24H, OCH₂ (G1)), 5.60–5.92 (m, 24H, =CH (G1)). ^{13}C NMR (ppm, $CDCl_3$): δ = -1.53 (SiMe (G0)), 1.30, 8.30 (SiCH₂ (G0)), 12.92 (CH₃ (EMI)), 16.53 (CH₃ (G1)), 31.05 (CH₂ (EMI)), 33.13, 39.16, 41.96, 44.73 (CH (G1)), 62.61, 65.64 (OCH₂ (G1)), 128.30, 129.90, 134.22, 134.89 (=CH (G1)), 177.02, 177.16 (C=O (G1)). GPC: PDI (M_w/M_n) = 1.000 (2448/2443), R_t = 17.43 min. Anal. calc. for $C_{156}H_{220}N_{12}O_{40}Si_8$ (M_w : 3124): C, 59.92; H, 7.04; N, 5.37. Found: C, 59.35; H, 6.51; N, 5.35%.

3.8. G1-12NQ

For the preparation of G1-12NQ, 0.12 g (0.13 mmol) of G1-12 HD, 0.45 g (2.84 mmol) of 1,4-naphthoquinone and 25 ml of toluene have been used and refluxed for 24 h. The 1,4-naphthoquinone free-product were obtained by washing the reaction mixture with ethanol and chloroform. Yield: 0.43 g (0.12 mmol, 92%) as brown precipitate. 1H NMR (ppm, $CDCl_3$): δ = 0.12 (s, 12H, SiMe (G0)), 0.30–0.53 (m, 16H, SiCH₂ (G0)), 0.53–0.80 (m, 36H, CH₃ (G1)), 2.42–2.80 (m, 24H, CH (G1)), 3.25–3.69 (m, 24H, CH (G1)), 3.88–4.26 (m, 24H, OCH₂ (G1)), 5.38–5.90 (m, 24H, =CH (G1)), 7.45–8.15 (m, 48H, Ph (NQ)). ^{13}C NMR (ppm, $CDCl_3$): δ = -1.41 (SiMe (G0)), 1.16, 7.75 (SiCH₂ (G0)), 18.37 (CH₃ (G1)), 32.02, 47.05, 46.64, 51.85 (CH (G1)), 63.84 (OCH₂ (G1)), 125.88, 126.39, 133.54, 134.12 (=CH, G1), 125.33, 130.90, 135.15, 137.34 (Ph (NQ)), 197.90, 198.92 (C=O (G1)). Anal. calc. for $C_{204}H_{208}$ -

$O_{40}Si_8$ (M_w : 3520): C, 69.55; H, 5.91. Found: C, 69.02; H, 5.84%. GPC: PDI (M_w/M_n) = 1.003 (2378/2370), R_t = 17.56 min.

3.9. G1-12TC

For the preparation of G1-12TC, 0.06 g (0.037 mmol) of G1-12 HD, 0.087 g (0.68 mmol) of tetracyanoethylene and 25 ml of toluene have been used, and stirred at room temperature for one day. The pure product was obtained by recrystallization in chloroform. Yield: 0.11 g (0.034 mmol, 91%) as yellow precipitate. 1H NMR (ppm, $CDCl_3$): δ = 0.19 (s, 12H, SiMe (G0)), 0.55–0.99 (m, 16H, SiCH₂ (G0)), 1.48–1.76 (m, 36H, CH₃ (G1)), 3.13–3.53 (m, 24H, CH (G1)), 4.10–4.45 (m, 24H, OCH₂ (G1)), 5.80–6.73 (m, 24H, =CH (G1)). ^{13}C NMR (ppm, $CDCl_3$): δ = 0.374 (SiMe (G0)), -1.391, 7.11 (SiCH₂ (G0)), 17.51 (CH₃ (G1)), 37.59, 39.27, 43.41 (CH (G1)), 63.18 (OCH₂ (G1)), 109.96, 110.36, 111.45, 112.09 (CN (G1)), 121.20, 128.43 (=CH (G1)). Anal. calc. for $C_{156}H_{136}N_{48}O_{16}Si_8$ (M_w : 3160): C, 59.24; H, 4.30; N, 21.26. Found: C, 59.14; H, 4.26; N, 20.94%. GPC: PDI (M_w/M_n) = 1.000 (2579/2577), R_t = 17.21 min.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2005.07.079](https://doi.org/10.1016/j.jorganchem.2005.07.079).

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