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Diels–Alder reaction of anthracene on carbosilane dendrimer

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Abstract

The dendritic macromolecule with 4, 8, 16 and 32 bicyclo end groups on the periphery has been created by the Diels–Alder reaction of anthracene and maleimide. The dendritic skeleton with triple bonds has been prepared by the hydrosilation and the alkynylation of bis(phenylethynyl)dimethylsilane as a core. The peripheral anthracene on dendrimers has been substituted by the reaction of chlorosilyl groups containing dendritic generations and 9-anthracenecarbinol. NMR and MALDI-TOF mass spectrum has characterized these Diels–Alder products.
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Keywords: Dendrimer; Silane; Diels–Alder; Hydrosilation; Anthracene

1. Introduction

Dendrimers with unique functional groups have been prepared by using two or three iterative reaction mechanisms [1]. The carbosilane dendrimers, synthesized by the use of multifunctional molecules as a core and chlorosilanes as progressing units, have increased tendency in the research area at the last decade [2–5]. In general, the reactions for the preparation of carbosilane dendrimers such as hydrosilation or alkenylation as well as alkynylation have progressed to almost quantitative yields. Moreover, side reactions such as α-addition or dehydrogenation reaction hasn't been observed in the reaction [6–8]. This is the most important point for the preparation of carbosilane dendrimers because the yield of the reactions has greatly influenced the purity according to the unimolecular property of dendrimers. Dendrons with irregularly developed branches are very difficult to be removed from a unimolecular dendritic group. In our previous results, the preparation of dendrimers by the use of the two-reaction pathways such as hydrosilation and alkynylation has revealed very high yields [4].

Reactions that create a new bond between elements as well as metal–carbons are very important in chemistry because they can be used for the purpose of the function of molecules and convert into the large one. DA reaction is a general concept for the addition of functional groups in organic synthesis. The reaction of anthracene on the dendritic periphery and ene moiety can be introduced to the bicyclo products known as Diels–Alder cycloadduct, one of useful methods for the addition of functional groups on dendritic surface [9]. The reaction of anthracene on dendritic periphery with maleimide as ene has produced DA products on dendritic surface with high yield (Scheme 1). In this report, we would like to show the demonstration of DA reaction on ethynylsilane dendrimers. The ethynylsilane dendrimers are relatively stabler than siloxane dendrimers against acid and base. The ethynylsilane dendrimers are more useful than the siloxane based denrimers to the measurement of M^+ ion by MALDI mass.

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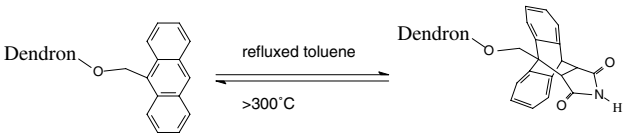
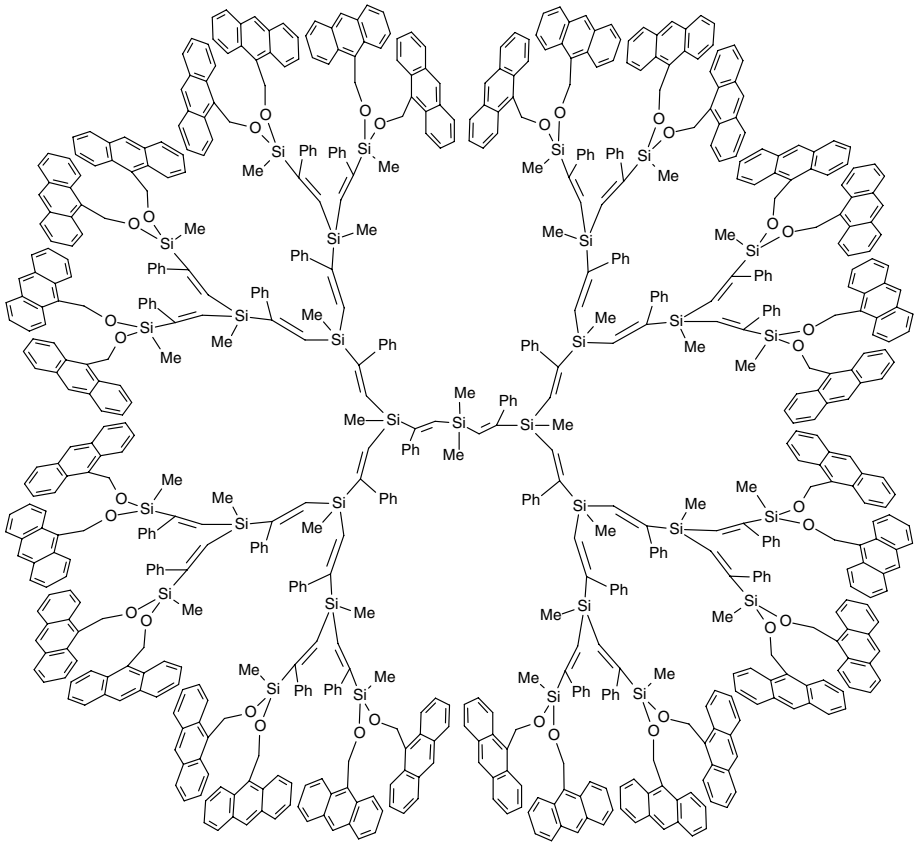


Scheme 1.

2. Results and discussion

The preparation of carbosilane dendrimers with triple bonds has started by the use of bis(phenylethnyl)dimethylsilane as a core, and dichloromethylsilyl groups and phenylethynyl groups as progressing units [4d]. The anthracene group on dendritic periphery has been substituted by the reaction of chlorosilyl groups on dendrimers and 9-anthracenecarbinol. The first generation with 4-ethynyl groups (G1) has been prepared by the reaction of hydrosilation of a core molecule (G0) with dichloromethylsilane and continual substitution of phenylethynyl groups into the chlorosilylated generation (G1-4Cl). The preparative methods of ethynyl dendrimers have been created by our previous works [8]. The yield of the reactions was almost quantitative. The reaction of chlorosilyl groups containing dendrimers and 9-anthracenecarbinol has progressed to G*n*-*m*A (n = 1–4; m = 4, 8, 16, 32) type dendrimers with anthracene by eliminating TMEDA-HCl salt with high yield. Purified dendrimers with anthracene, G*n*-*m*A, have been obtained by chromatography using a silica gel–toluene combination (Scheme 2). The excess of anthracenecarbinol and the rest of TMEDA have been removed by this method with the use of mixed solvents such as toluene and chloroform. The dendrimers have been characterized from ^{1}H NMR, MALDI mass as well as elemental analysis. All the generations of dendrimers (G*n*-*m*A) exhibited to be readily soluble in a wide range of solvents including toluene, diethyl ether, chloroform, etc. Yields were very high (over 90%, obtained yields after chromatographic attachments). The ^{13}C NMR spectra of the G*n*-*m*A type dendrimers have provided a unique property through the first to the fourth generation (Fig. 1). The MALDI mass spectrum of G1-4A in Fig. 2 has shown 6 signals. The 1200 amu is molecular ion peak with sodium $(M + Ma)^+$ and 1009 amu $(M + Na - anthracenemethylene)^+$ and 819 amu $(M + Na - 2\ anthracenemethylene)^+$ are fragmentation of $(M + Na)^+$ ions. The small peak 1177 amu (M^+), 986 amu $(M - anthracenemethylene)^+$ and 796 amu $(M - 2\ anthracenemethylene)^+$ are fragmentation of the molecular ion peak (M^+). The mass spectrum of G2-8A and G3-16A has shown the same fragmentation tendency (Fig. 3). The m/z value of G2-8A to G4-32A has shown signals containing the



Scheme 2. Schematic planner view of G4-32A.

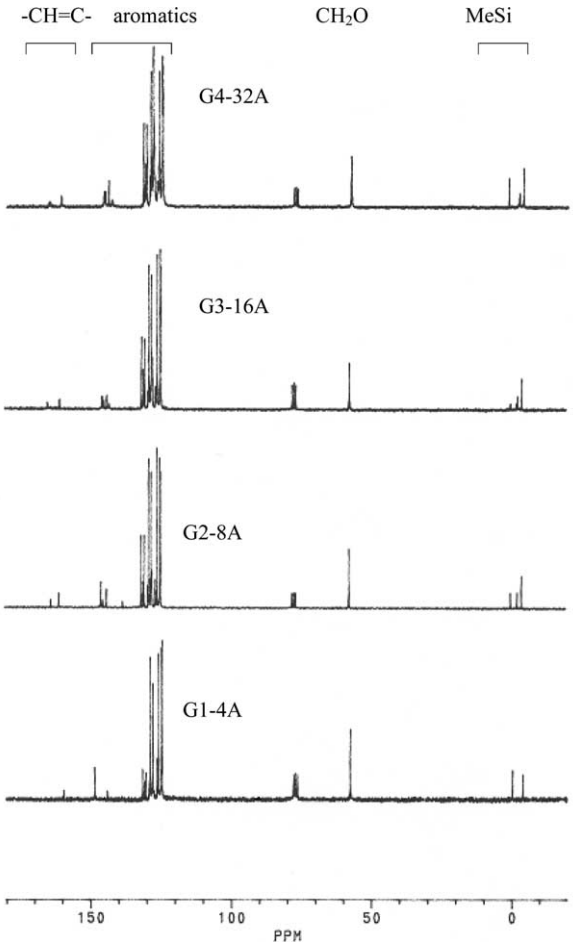


Fig. 1. ^{13}C NMR spectrum of G*n*-*m*A.

molecular ion peak with one sodium metal (Figs. 2–5 and Table 1). In addition, the elemental analysis has shown very near value for the calculated one (see Section 3).

The Diels–Alder reaction of anthracene on dendritic periphery with maleimide has been performed under the reflux condition in toluene. The reaction rate has decreased according to increasing generations. The preparation of the first generational DA product G1-4AM and G2-8AM has been completely made under the 10 h reflux condition. And the preparation of G3-16AM and G3-32 AM has been made under the overnight reflux condition. The excess of maleimide in the process of preparation of G1-4AM has been removed by washing with mixed solvents such as pentane and ethanol. After removing the excess reactants, the purification of the product has progressed under chromatography with a silica gel–toluene combination. Other higher generations of DA products (G2-8AM, G3-16AM and G4-32AM) have been used for the same reaction path and purification methods. In all these cases, the synthetic process has been monitored by ^{1}H NMR which observed disappearance of characteristic anthracene signals at aromatic area (6.6–8.4 ppm) and conversely observed the formation of new signals at the bicyclo area (4.8–5.5 ppm). The ^{13}C NMR spectra of Diels–Alder reaction have progressed G*n*-*m*AM dendrimers providing a unique property through the first to the fourth generations, which can be easily detected by characteristic signals. The MALDI-mass spectra of DA products G*n*-*m*AM have mainly shown one molecular ion peak at 1588 amu for G1-4AM, 3384 amu for G2-8AM, 6976 amu for G3-16AM and 14,173 amu for G4-32AM (Scheme 3) due to the molecular ion peak with one sodium ion (Figs. 2–5). The MALDI mass spectra of G*n*-*m*AM with Diels–Alder products have been shown relatively smaller mass fragmentation. The elemental analysis has shown very near value for the calculated one (Table 1).

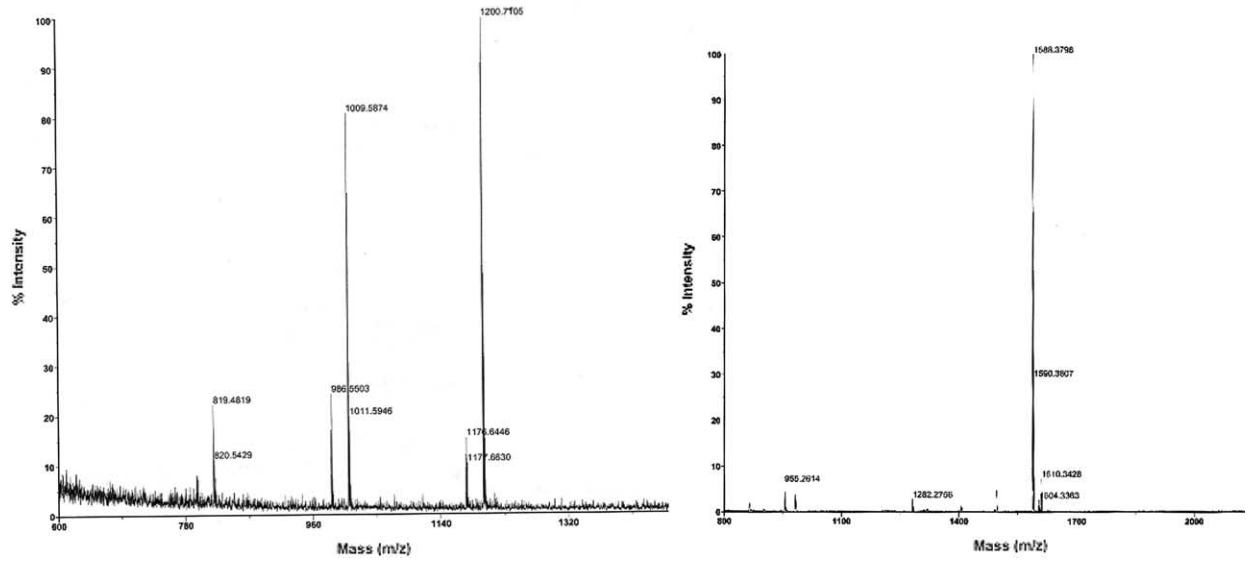


Fig. 2. MALDI mass spectrum of G1-4A (left) and G1-4AM (right).

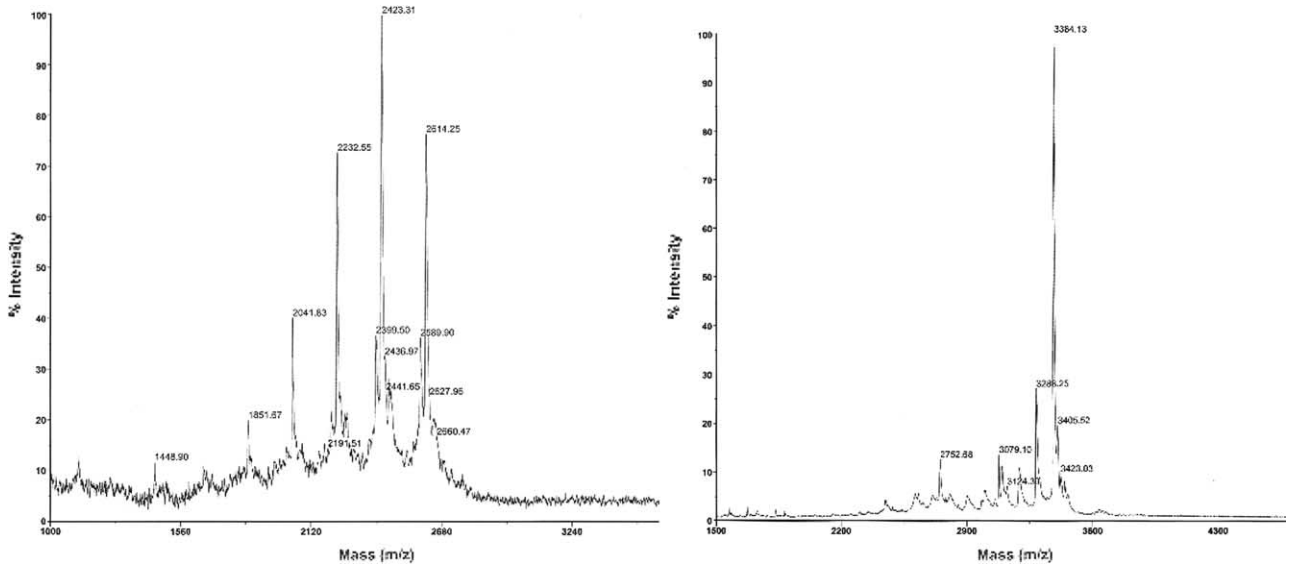


Fig. 3. MALDI mass spectrum of G2-8A (left) and G2-8AM (right).

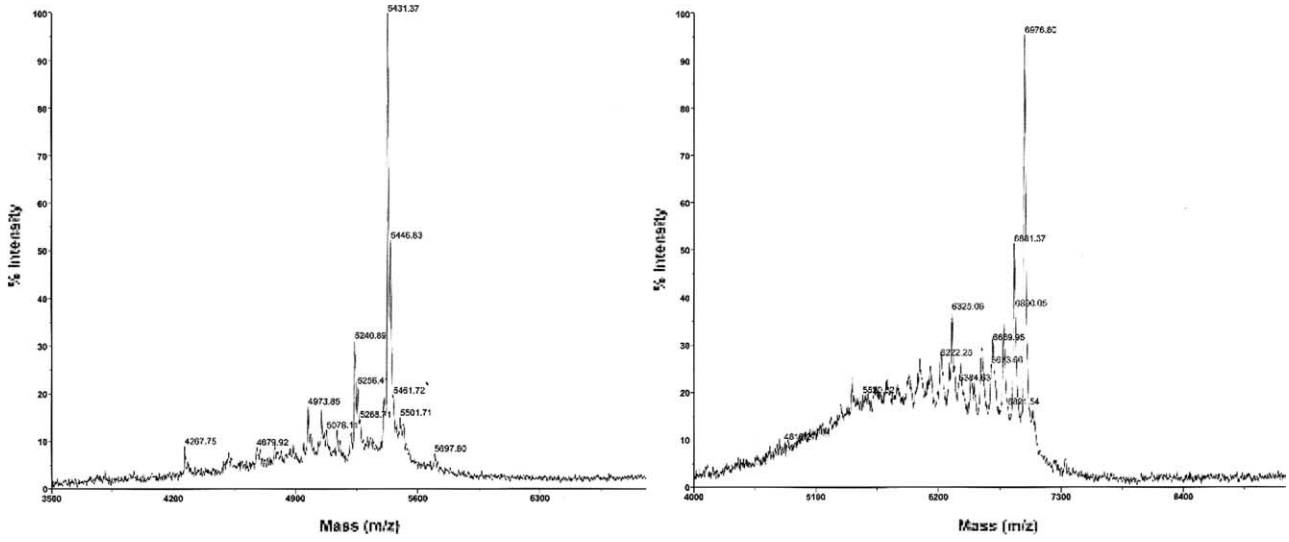


Fig. 4. MALDI mass spectrum of G3-16A (left) and G3-16AM (right).

To summarize, we have demonstrated the versatile synthesis of dendrimers with Diels–Alder reaction that enables new synthetic approach for the addition of functional groups on dendritic periphery. These acene type diene can be potentially used for the family of Diels–Alder reaction on dendritic periphery.

3. Experiment

All the reactions have been performed under dried N_2 atmosphere. The NMR spectra have been recorded on Bruker AC-200 Spectrometer. The Busan and Daejon Branches of the Korean Basic Science Institute (KBSI) performed MALDI mass and elemental analysis. An HP 8452A Diode Array UV/Vis Spectrophotometer has obtained UV spectral data. The following abbreviations have been used in these experiments: G*n*-*m*A refers to the dendrimers with anthracene on periphery; G*n*-*m*AM refers to the dendrimers with Diels–Alder products.

3.1. G1-4A

Well-dried 1.07 g (5.13 mmol) of 9-anthracenecanbinol was dissolved in 50 ml of toluene and added to

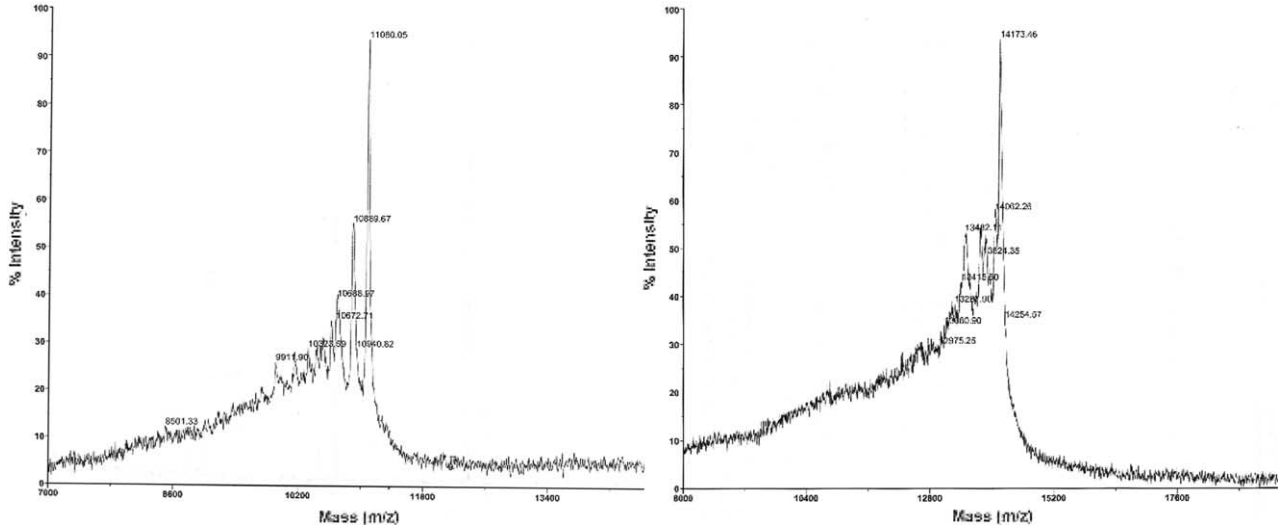


Fig. 5. MALDI mass spectrum of G4-32A (left) and G4-32AM (right).

Table 1
MALDI mass data

Entry	Formula	M^+ (g/mol)	
		Calc.[a]	Found
G1-4A[b]	$C_{80}H_{68}O_4Si_3$	1177	1200 $(M + Na)^+$
G2-8A[c]	$C_{176}H_{148}O_8Si_7$	2587	2614 $(M + Na)^+$
G3-16A[d]	$C_{368}H_{308}O_{16}Si_{15}$	5407	5431 $(M + Na)^+$
G4-32A	$C_{752}H_{628}O_{32}Si_{31}$	11,047	11,080 $(M + Na)^+$
G1-4AM	$C_{96}H_{80}N_4O_{12}Si_3$	1565	1588 $(M + Na)^+$
G2-8AM	$C_{208}H_{172}N_8O_{24}Si_7$	3364	3384 $(M + Na)^+$
G3-16AM	$C_{432}H_{356}N_{16}O_{48}Si_{15}$	6961	6976 $(M + Na)^+$
G4-32AM	$C_{880}H_{724}N_{32}O_{96}Si_{31}$	14,154	14,173 $(M + Na)^+$

[a] Calc., calculated mass
[b] 1009 $(M + Na - anthracenemethylene)^+$, 819 $(M + Na - 2$ anthracenemethylene$)^+$, 1177 (M^+), 986 $(M - anthracenemethylene)^+$, 796 $(M - 2$anthracenemethylene$)^+$
[c] 2614 $(M + Na)^+$, 2423 $(M + Na - anthracenemethylene)^+$, 2041 $(M + Na - 2$ anthracenemethylene$)^+$
[d] *[3]: 5431 $(M + Na)^+$, 5240 $(M + Na - anthracenemethylene)^+$

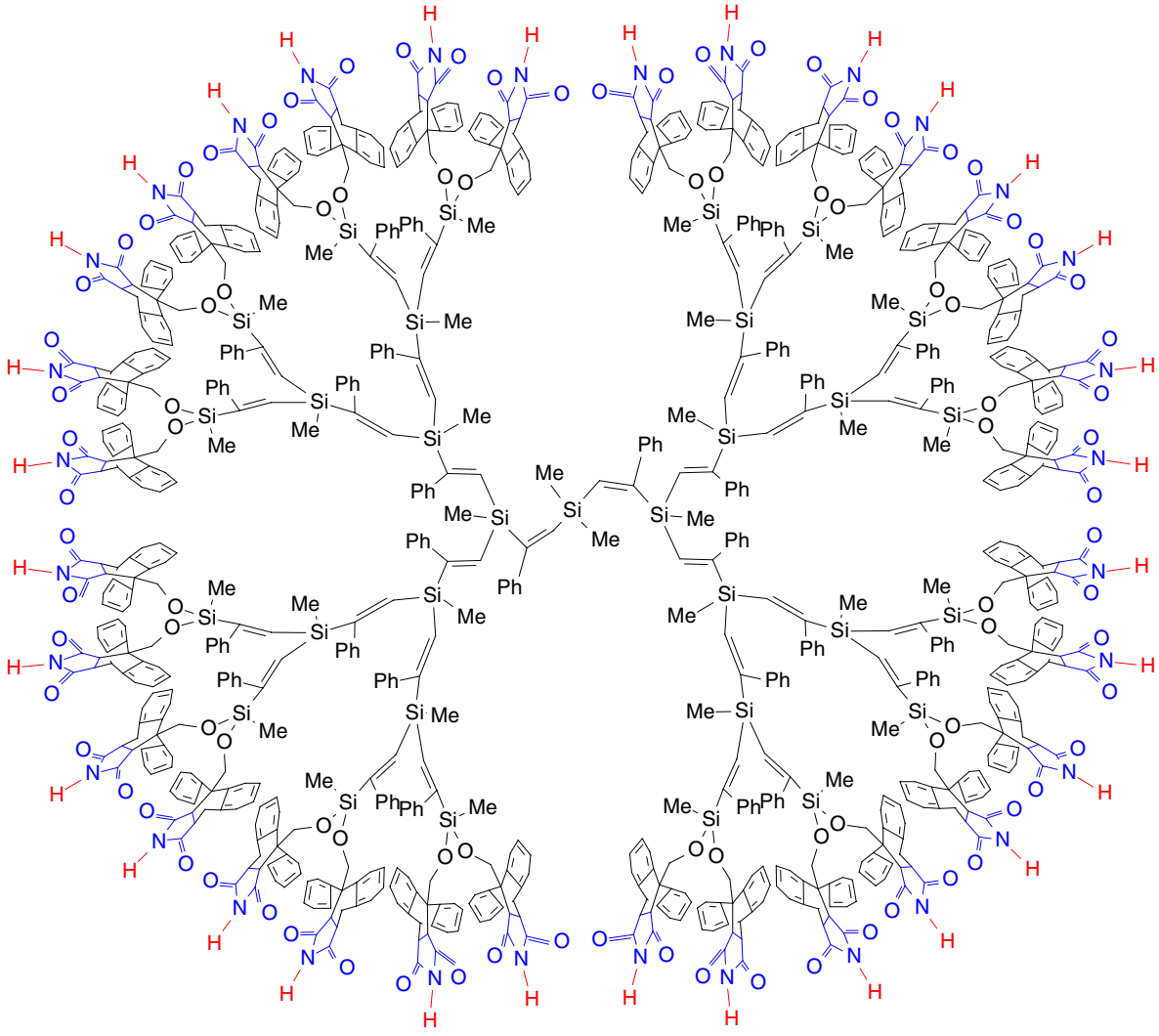
2 ml of TMEDA (13.34 mmol). 0.57 g (1.16 mmol) of G1P-4Cl was added to the reaction medium and warmed at 60 °C for 30 min. After cooling the reaction bath, the salt must be removed by filtration. Chromatography with silica gel, mixed solvents with toluene, and chloroform 2 to 1 purified the reaction product. 1.32 g (1.10 mmol, 96%) of light yellow solid was obtained. ^{1}H 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 $C_{80}H_{68}O_4Si_3$ (M_w: 1177.67): C, 81.59%, H, 5.82%. Found: C, 81.25%, H, 5.82%. UV–Vis, $\lambda_{max} = 258$ nm, $\varepsilon_{max} = 1.62 \times 10^5$.

3.2. G2-8A

The same method as that of G1-4A was used in the reaction of 1.40 g (6.72 mmol) of anthracenecarbinol, 2 ml of TMEDA, and 0.85 g (0.70 mmol) of G2P-8Cl. Yield: 1.68 g (0.65 mmol, 93%) of light yellow solid. ^{1}H 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 (G1P)), 6.59 (s, 4H, CH=C (G2P)), 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 (G1)), −0.25 (SiMe (G0)), 57.34 (OCH_2), 124.46, 124.77, 125.72, 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 $C_{176}H_{148}O_8Si_7$ (M_w: 2587.70): C, 81.69%, H, 5.76%. Found: C, 81.38%, H, 5.72%. UV–Vis, $\lambda_{max} = 258$ nm, $\varepsilon_{max} = 4.07 \times 10^5$.

3.3. G3-16A

The same method as that of G1-4A was used in the reaction of 0.92 g (4.42 mmol) of anthracenecarbinol, 2 ml of TMEDA, and 0.61 g (0.23 mmol) of G3P-16Cl. Yield: 1.20 g (0.22 mmol, 97%) of light yellow solid. ^{1}H NMR (ppm, $CDCl_3$): $\delta = -0.82$ to −0.48 (m, 24H, SiMe (G0–G2)), −0.19 to 0.11 (m, 24H, SiMe (G3)), 5.02–5.48 (m, 32H, OCH_2), 6.01 (s, 2H, CH=C (G1P)), 6.18 (s, 4H, CH=C (G2P)), 6.50 (s, 8H, CH=C (G3P)), 6.60–6.91, 6.91–7.12, 7.12–7.50, 7.67–7.90, 7.90–



Scheme 3. Schematic planner view of G4-32AM.

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 $C_{368}H_{308}O_{16}Si_{15}$ (M_w: 5407.75): C, 81.74%, H, 5.74%. Found: C, 81.07%, H, 5.72%. UV–Vis, $\lambda_{max} = 258$ nm, $\varepsilon_{max} = 1.03 \times 10^6$.

3.4. G4-32A

The same method as that of G1-4A was used in the reaction of 1.29 g (6.18 mmol) of anthracenecarbinol, 2 ml of TMEDA, and 0.85 g (0.16 mmol) of G2P-8Cl. Yield: 1.62 g (0.15 mmol, 92%) of light yellow solid. ^{1}H NMR (ppm, $CDCl_3$): $\delta = -0.80$ to -0.40 (m, 48H, SiMe), -0.19 to 0.12 (m, 48H, SiMe), 5.00–5.52 (m, 64H, OCH_2), 6.01 (s, 2H, CH=C (G1P)), 6.09 (s, 4H, CH=C (G2P)), 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 $C_{752}H_{628}O_{32}Si_{31}$ (M_w: 11,047.08): C, 81.76%, H, 5.73%. Found: C, 81.78%, H, 5.71%. UV–Vis, $\lambda_{max} = 258$ nm, $\varepsilon_{max} = 1.44 \times 10^6$.

3.5. G1-4AM

0.16 g (1.63 mmol) of Maleimide and 0.40 g (0.34 mmol) of G1-4A dissolved in toluene and the reaction mixture reflux for 10 h. The excess of maleimide

was removed by washing with mixed solvent pentane and ethanol 5 to 1. 0.51 g (0.32 mmol, 96%) of white solid was yielded. ^{1}H NMR (ppm, $CDCl_3$): $\delta = -0.34$ to -0.27 (m, 6H, SiMe (G0)), 0.66–0.68 (m, 6H, SiMe (G1)), 4.42–4.83 (m, 8H, OCH_2), 2.82–3.57, 4.83–5.47 (m, 16H, CH), 6.73–7.02, 7.02–7.31, 7.31–7.50, 7.50–7.80 (CH=C, Ph, anthracene, maleimide). ^{13}C NMR (ppm, $CDCl_3$): $\delta = -5.37$, -5.19 (SiMe (G1)), -0.34, 0.99 (SiMe (G0)), 45.54, 46.47, 48.98, 49.35 (CH), 60.42 (OCH_2), 121.93, 122.21, 123.49, 124.26, 124.45, 124.67, 125.17, 125.67, 126.16, 126.26, 126.42, 126.71, 127.48, 127.89, 128.05, 128.65, 130.18, 130.64, 131.26, 138.81, 138.91, 138.97, 139.13, 139.21, 141.80, 141.91, 142.18, 142.29, 144.00 (Ph, anthracene, maleimide), 149.03, 159.87 (CH=C), 176.27, 176.38, 177.17, 177.25 (C=O). Anal. Calc. for $C_{96}H_{80}N_4O_{12}Si_3$ (M_w = 1565.95): C, 73.63%, H, 5.15%, N, 3.58%. Found: C, 72.93%, H, 5.19%, N, 3.42%. UV–Vis, λ_{max} = 245 nm, $\varepsilon_{max} = 2.52 \times 10^7$.

3.6. G2-8AM

The same method as that of G1-4AM was used in the reaction of 0.16 g (1.63 mmol) of maleimide and 0.40 g (0.34 mmol) of G2-8A. Yield: 0.51 g (0.32 mmol, 96%) of light yellow solid. ^{1}H NMR (ppm, $CDCl_3$): $\delta = -0.78$ to -0.40 (m, 12H, SiMe (G0–G1)), -0.50 to 0.80 (m, 12H, SiMe (G2)), 4.40–4.75 (m, 16H, OCH_2), 2.75–3.49, 4.75–5.42 (m, 32H, CH), 6.01–6.24, 6.46–6.73, 6.73–7.12, 7.12–7.60, 7.60–8.18, 8.18–8.39 (CH=C, Ph, anthracene, maleimide). ^{13}C NMR (ppm, $CDCl_3$): $\delta = -5.40$ (SiMe (G2)), -2.98 (SiMe (G1)), -0.43 (SiMe (G0)), 45.44, 46.16, 48.91, 49.31 (CH), 60.25 (OCH_2), 121.91, 123.48, 124.26, 125.27, 126.22, 127.69, 128.19, 129.00, 134.99, 137.84, 138.96, 141.83, 142.23, 143.66, 144.98 (Ph, anthracene, maleimide), 146.10, 147.11, 160.63, 161.98 (CH=C), 176.32, 177.34 (C=O). Anal. Calc. for $C_{208}H_{172}N_8O_{24}Si_7$ (3364.09): C, 74.26%, H, 5.15%, N, 3.33%. Found: C, 73.89%, H, 5.33%, N, 2.74%. UV–Vis, λ_{max} = 245 nm, $\varepsilon_{max} = 8.29 \times 10^7$.

3.7. G3-16AM

The same method as that of G1-4AM was used in the reaction of 0.17 g (1.77 mmol) of maleimide and 0.50 g (0.34 mmol) of G3-16A. Yield: 0.54 g (0.092 mmol, 84%) of white solid. ^{1}H NMR (ppm, DMSO): $\delta = -1.20$ to -0.59 (m, 24H, SiMe (G0–G2)), 0.20–0.70 (m, 24H, SiMe (G3)), 4.31–4.63 (m, 32H, OCH_2), 2.72–3.60, 4.63–5.40 (m, 64H, CH), 5.74–6.26, 6.26–6.50, 6.50–7.10, 7.10–7.80 (CH=C, Ph, anthracene, maleimide), 10.77 (s, 16H, NH). ^{13}C NMR (ppm, $CDCl_3$): $\delta = -5.62$ (SiMe (G3)), -2.66 (SiMe (G2)), -2.31 (SiMe (G0)), -0.03 (SiMe (G1)), 45.51, 46.17, 48.92, 49.31 (CH), 60.24 (OCH_2), 121.78, 122.11, 123.78, 124.26, 126.55, 127.37, 127.65, 127.96, 134.09, 136.31, 138.26, 138.40, 138.72, 140.74, 140.86, 141.50, 143.34, 144.71, 145.16, 145.41 (Ph, anthracene, maleimide), 146.11, 147.10, 160.64, 161.97 (CH=C), 169.55, 170.53 (C=O). Anal. Calc. for $C_{432}H_{356}N_{16}O_{48}Si_{15}$ (M_w = 6961.06): C, 74.54%, H, 5.15%, N, 3.22%. Found: C, 74.60%, H, 5.38%, N, 3.08%. UV–Vis, λ_{max} = 245 nm, $\varepsilon_{max} = 3.48 \times 10^8$.

3.8. G4-32AM

The same method as that of G1-4AM was used in the reaction of 0.27 g (2.78 mmol) of maleimide and 0.80 g (0.072 mmol) of G4-32A. Yield: 0.92 g (0.065 mmol, 90%) of white solid. ^{1}H NMR (ppm, DMSO): $\delta = -1.28$ to -0.57 (m, 48H, SiMe (G0–G3)), -0.20 to 0.68 (m, 48H, SiMe (G4)), 4.19–4.78(m, 64H, OCH_2), 2.60–3.80, 4.78–5.44 (m, 128H, CH), 5.76–6.17, 6.17–6.98, 6.98–7.80 (CH=C, Ph, anthracene, maleimide), 10.70 (s, 32H, NH). ^{13}C NMR (ppm, $CDCl_3$): $\delta = -5.48$ (SiMe (G4)), -1.88 (SiMe (G2–G3)), 0.47 (SiMe (G0)), 1.31 (SiMe (G1)), 45.53, 46.17, 48.97, 49.33 (CH), 60.23 (OCH_2), 121.81, 123.93, 124.28, 125.33, 126.58, 127.01, 127.43, 128.02, 138.41, 140.87, 141.52, 143.42, 144.91, 145.96 (Ph, anthracene, maleimide), 146.24, 147.12, 160.62, 161.90 (CH=C), 169.58, 170.51 (C=O). Anal. Calc. for $C_{880}H_{724}N_{32}O_{96}Si_{31}$ (14154.49): C, 74.68%, H, 5.16%, N, 3.17%. Found: C, 73.78%, H, 5.18%, N, 3.04%. UV–Vis, λ_{max} = 245 nm, $\varepsilon_{max} = 1.69 \times 10^9$.

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References

[1] (a) For recent reviews F. Vögtle, S. Gestermann, R. Hesse, H. Schwierz, B. Windisch, Prog. Polym. Sci. 25 (2000) 987;
(b) D. Astruc, F. Chardac, Chem. Rev. 101 (2001) 2991;
(c) J.P. Majoral, A.M. Caminade, Chem. Rev. 99 (1999) 845;
(d) K. Inoue, Prog. Polym. Sci. 25 (2000) 453;
(e) A.W. Bosman, H.M. Janssen, E.W. Meijer, Chem. Rev. 99 (1999) 1665.
[2] R. van Heerbeek, J.N.H. Reek, P.C.J. Kamer, P.W.N.M. van Leeuwen, Tetrahedron Lett. 40 (1999) 7839.
[3] H. Frey, C. Shlenk, Top. Curr. Chem. 210 (2000) 69.
[4] (a) C. Kim, J. Park, J. Organomet. Chem. 629 (2001) 194;
(b) C. Kim, K. Jeong, I. Jung, J. Polym. Sci. A: Polym. Chem. 38 (2000) 2749;
(c) C. Kim, I. Jung, J. Organomet. Chem. 599 (2000) 208;
(d) C. Kim, M. Kim, J. Organomet. Chem. 563 (1998) 43.
[5] C.-O. Turrin, J. Chiffre, D. de Montauzon, G. Balavoine, E. Manoury, A.-M. Caminade, J.-P. Majoral, Organometallics 21 (2002) 1891.
[6] J.Y. Corey, Adv. Silicon Chem. 1 (1991) 327.

[7] J. Stein, N.L. Lewis, Y. Gao, R.A. Scott, J. Am. Chem. Soc. 121 (1999) 3693.
[8] S. Sakaki, N. Mizoe, M. Sugimoto, Organometallics 17 (1998) 2510.
[9] (a) J.R. McElhanon, D.R. Wheeler, Org. Lett. 3 (2001) 2681;
(b) C. Kim, H. Kim, K. Park, J. Polym. Sci. A: Polym. Chem. 42 (2004) 2155.