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Controlled Cyclotrimerization in Hyperbranched Polymer Synthesis

Masayoshi Higuchi, Hirohiko Kanazawa, Masanori Tsuruta, and Kimihisa Yamamoto*,†

Department of Chemistry, Faculty of Science & Technology, Keio University, Yokohama, 223-8522 Japan

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ABSTRACT: Cyclization in hyperbranched polymer synthesis was first controlled on the basis of a steric effect using a Lewis acid with a bulky ligand. Only phenylazomethine oligomers having a cyclic structure were formed during the polymerization of 4,4′-diaminobenzophenone in the presence of $TiCl_4(THF)_2$ as a Lewis acid with bulky ligands. The structure of a cavity in an isolated cyclic oligomer was determined by X-ray crystal analysis. Controlled cyclization is applied for hyperbranched polymer synthesis, and a novel dendrimer with a cyclic structure was quantitatively obtained via controlled cyclization on the basis of a steric effect using a monomer with a bulky dendron.

Introduction

Hyperbranched polymers[1] have attracted the attention of many researchers because of the unusual properties in comparison to conventional linear polymers. In general, hyperbranched polymers are synthesized by the polymerization of multifunctional compounds such as AB_2 type monomers, but the intramolecular macrocyclization is also confirmed by TOF-MS measurements.[2] The cyclization is undesirable for hyperbranched polymer synthesis, but highly controlled cyclization has a possibility to give novel functional materials or synthetic methods of hyperbranched polymers. From the viewpoint of functional materials, multifunctional cyclic oligomers are attractive building blocks for supramolecular systems, because they have a cavity for ion reception or molecular recognition and functional groups that can combine with other compounds by chemical and/or hydrogen bonds. However, the isolation of a single cyclic oligomer in hyperbranched polymerization has not been reported to the best of our knowledge, because the yield of each cyclic oligomer is too low to isolate due to further polymerization between the cyclic oligomers with monomers in the reaction mixture. We first controlled cyclization in hyperbranched polymer synthesis on the basis of a steric effect using a Lewis acid with bulky ligands. A multifunctional cyclic oligomer was isolated, and the structure including a cavity was determined by X-ray crystal analysis. Moreover, a highly selective synthetic method of hyperbranched polymers via controlled cyclization was investigated, and we revealed that a dendrimer having a cyclic structure was quantitatively obtained on the basis of a steric effect using a monomer with a bulky dendron.

Results and Discussion

p-Toluenesulfonic acid (PTS) and $TiCl_4$ are good dehydration agents for cyclization during the linear polymerization of 4-aminobenzophenone derivatives,[3] but both acids were useless for the cyclic oligomerization of 4,4′-diaminobenzophenone, which is an AB_2 type monomer; the dehydration did not proceed in the presence of PTS, because the electrophilicity in the carbonyl carbon of the monomer is reduced by the π-conjugation expanded to the two aminophenyl groups. $TiCl_4$ is a powerful dehydration agent, but the dehydration led to the formation of only the insoluble phenylazomethine polymer due to the random polymerization. Unlike PTS and $TiCl_4$, in the presence of $TiCl_4(THF)_2$,[4] which was formed by the rapid complexation of $TiCl_4$ with THF solvent, the preferential formation of phenylazomethine oligomers having one cyclic structure was confirmed by the TOF-MS spectrum of the crude products in the polymerization. This TOF-MS spectrum is much different from those of general hyperbranched polymerization; only peaks attributed to oligomers having one cyclic structure appeared in the spectrum (Figure 1a).[5] This result shows that the introduction of bulky THF groups in $TiCl_4$ strongly promotes the formation of the *Z*-conformational azomethine bonds by steric hindrance as shown in Figure 2, and as a result, only oligomers having a cyclic structure were obtained. The GPC result of the crude products also supports the composition ratio of the respective oligomers shown by TOF-MS analysis (Figure 1b).

The structure of novel trifunctional cyclic trimer (CPA-3a), which was formed via this one-pot synthesis, was determined by X-ray crystal analysis (Figure 3). The X-ray crystals of CPA-3a were obtained by the slow vapor diffusion of methanol into a THF solution of CPA-3a. As shown in Figure 3, the imine nitrogen atoms have enough space outside the molecule to combine with $TiCl_4(THF)_2$, which led to the preferential formation of the *Z*-conformational imine bond. The terminal amino group of CPA-3a promotes the 2-dimensional dimerization by the formation of a hydrogen bond with the core imine of the another molecule (the N−N distance: 3.20 Å).[6] The CPA-3a has a cavity (19.6 Å^2) similar to [2.2.2]-paracyclophane, which is a typical π-receptor for metal ions.

This cyclization method was also useful for cyclization during the linear polymerization of 4-aminobenzophenone. The reported yield[3] (20%) of the cyclic trimer in the presence of $TiCl_4$ was enhanced to a 51% yield by using $TiCl_4(THF)_2$. As a result, one way to control cyclization during the polymerization of both the AB_2 and AB type monomers was revealed to be using a Lewis acid with bulky ligands.

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* Corresponding author. E-mail yamamoto@chem.keio.ac.jp.
† KAST Project Leader.

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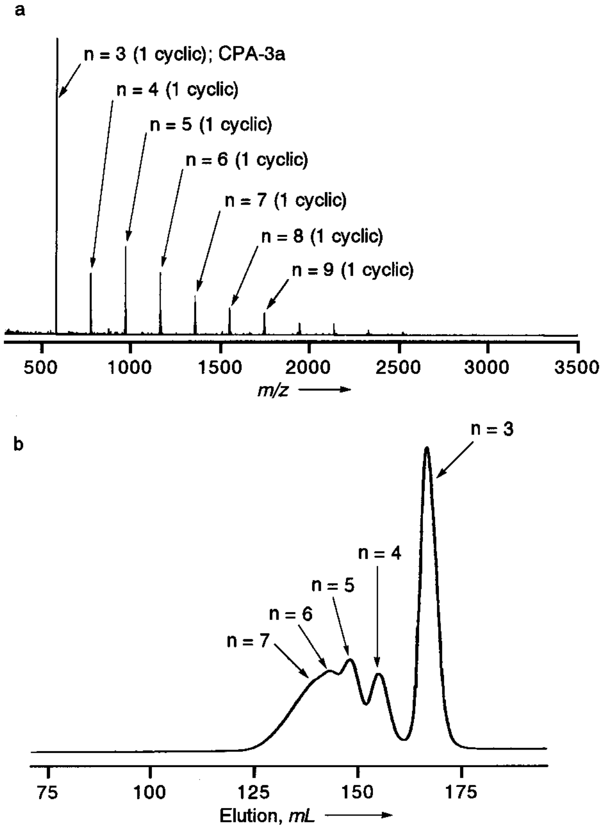

Figure 1. (a) TOF-MS spectrum and (b) GPC analysis of the crude products during the polymerization of 4,4′-diaminobenzophenone in the presence of $TiCl_4(THF)_2$.

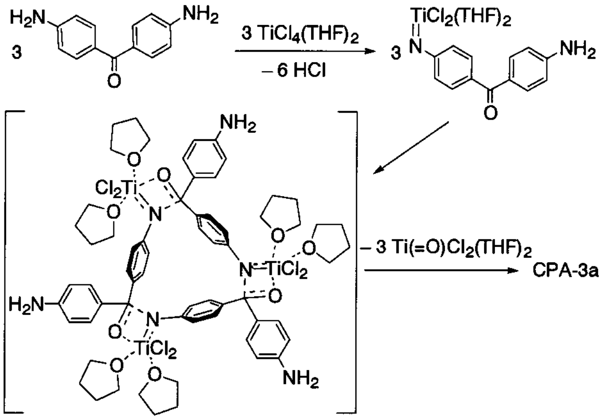

Figure 2. Controlled cyclization in the presence of $TiCl_4(THF)_2$.

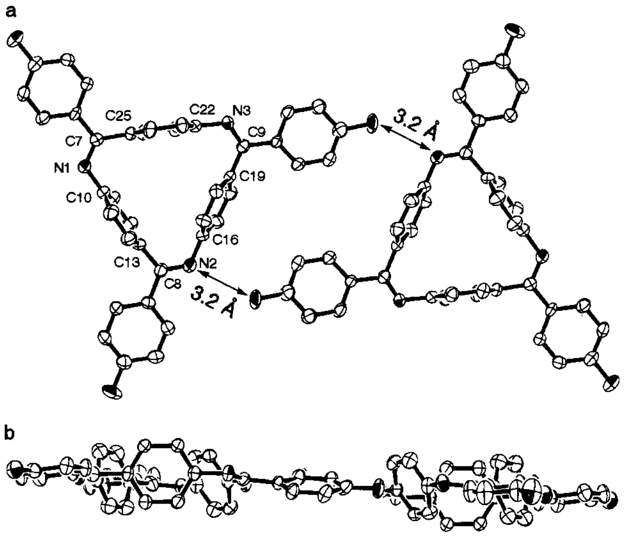

Figure 3. ORTEP figure of CPA-3a with 30% ellipsoid (hydrogen atoms are omitted). (a) Top view and (b) side view. Selected angles: N1–C7–C25, 122.0(6)°; C7–N1–C10, 120.0(6)°; N2–C8–C13, 123.6(6)°; C8–N2–C16, 118.6(5)°; N3–C9–C19, 122.3(6)°; C9–N3–C22, 120.9(6)°.

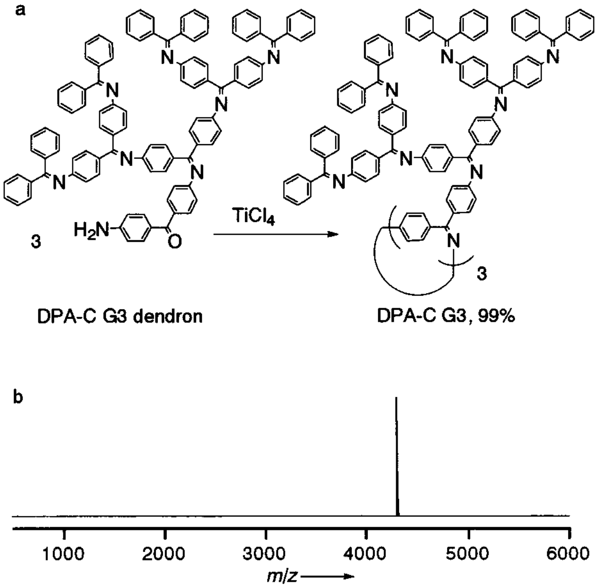

Figure 4. (a) Highly selective synthesis of DPA-C G3 via controlled cyclization and (b) the TOF-MS spectrum of DPA-C G3 (4302 $[M + H]^+$).

Moreover, hyperbranched polymer synthesis via controlled cyclization was investigated. Another way to control cyclization during the polymerization of AB type monomers is using a monomer with a bulky substituent such as a dioctylaminophenyl group.[3] This controlled cyclization was applied for synthesis of a perfectly hyperbranched polymer, that is, a dendrimer.[7] In the polymerization of 4-aminobenzophenone derivative having a DPA G3 dendron[8] as a bulky substituent, a novel dendrimer having a cyclic structure (DPA-C G3) was quantitatively obtained due to steric hindrance among the bulky dendrons (Figure 4a). The DPA-C G3 obtained by filtration was pure enough without further purification by column chromatography. The TOF-MS spectrum (Figure 4b) and GPC analysis ($M_w/M_n = 1.03$) show that DPA-C G3 is the sole compound with a single molecular weight. In the polymerization of 4-aminobenzophenone derivatives having DPA dendron G1 and G2 (DPA-C dendrons G1 and G2), the corresponding dendrimers having a cyclic structure (DPA-C G1 and G2) were obtained in 42% and 70% yields, respectively. These results show that the increase in the generation of a dendron enhances the yield of the corresponding dendrimer due to the steric hindrance between the bulky dendrons. The kinetic analysis using GPC in the polymerization of DPA-C G1 dendron revealed that the cyclotrimerization proceeds very rapidly and the formation of DPA-C G1 almost finishes within 10 min (Figure 5a,c). Interestingly, the linear trimer was not detected at all by TOF-MS measurement even in the crude solution at the reaction time for 1 min (Figure 5b). The absence of the linear trimer in the reaction mixture supports that the cyclic trimers are formed mainly via the one-step synthesis shown in Figure 2 rather than a

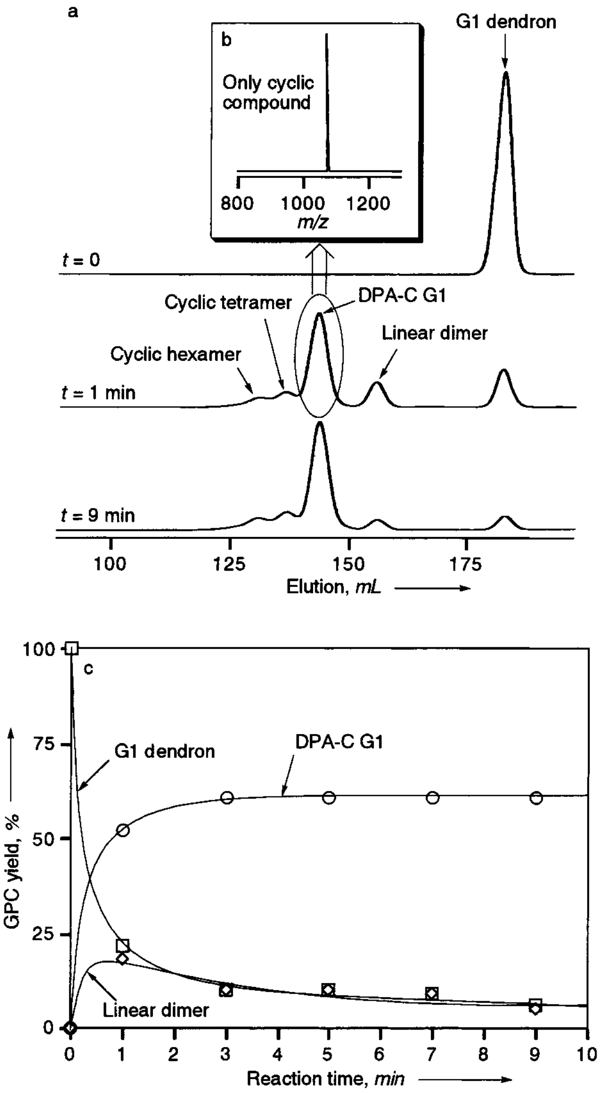

Figure 5. Kinetic analysis using GPC in the polymerization of DPA-C G1 dendron. (a) GPC elution curves at the reaction time for 0, 1, and 9 min and (b) the TOF-MS spectrum of the trimer. (c) The relationship between the yields of DPA-C G1, the G1 dendron, and linear dimer and the reaction time.

stepwise polymerization such as dimer ⇒ linear trimer ⇒ cyclic trimer.

Conclusion

Cyclization in hyperbranched polymer synthesis was first controlled on the basis of a steric effect using a Lewis acid with a bulky ligand, and the crystal structure of a multifunctional cyclic oligomer and the dimerization based on hydrogen bonds were revealed. Moreover, hyperbranched polymer synthesis via controlled cyclization was investigated, and a dendrimer having a cyclic structure was quantitatively synthesized on the basis of a steric effect using a monomer with a bulky dendron.

Experimental Section

Materials. All reagents were purchased from Aldrich, Merck, or Kanto Chemicals and were used without further purification. All reactions were carried out with dry, freshly distilled solvents under anhydrous conditions or in an inert atmosphere.

Synthesis of CPA-3a. $TiCl_4$ (0.270 g, 1.42 mmol) was added to a mixture of 4,4′-diaminobenzophenone (0.600 g, 2.83 mmol) and 1,4-diazabicyclo[2.2.2]octane (DABCO) (1.28 g, 11.4 mmol) in anhydrous THF (100 mL) under a nitrogen atmosphere. White fumes were generated upon the addition of $TiCl_4$. The reaction mixture was heated in an oil bath at 90 °C for 5 h. After cooling, $TiCl_4$ (0.270 g, 1.42 mmol) and DABCO (1.28 g, 11.4 mmol) were further added in the reaction mixture, and the solution was heated again in an oil bath at 90 °C for 10 h. Disappearance of the monomer was confirmed on TLC, and the precipitate was removed by filtration. The filtrate was concentrated; CPA-3a (0.108 g, 0.19 mmol, 20% yield) was isolated by silica gel column chromatography (dichloromethane: ethyl acetate = 1:0−1:2, including 1% Et_3N, $R_f = 0.3$ in the solution of ethyl acetate:dichloromethane = 1:2). CPA-3a: ^{1}H NMR (270 MHz, DMSO-d_6, TMS standard, ppm): δ 7.43 (d, J = 8.4 Hz, 6H), 6.68 (d, J = 8.1 Hz, 6H), 6.56 (d, J = 8.4 Hz, 6H), 6.39 (d, J = 8.1 Hz, 6H), 5.76 (s, 6H). ^{13}C NMR (67.5 MHz, DMSO-d_6, TMS standard, ppm): δ 169.36, 152.54, 151.77, 130.50, 130.32, 127.57, 125.32, 119.55, 112.81. IR (KBr): 3457 (ν_{as} NH$_2$), 3376 (ν_s NH$_2$), 1623 (ν C=N), 1586 (phenyl). EI-MS 582 [M]$^+$. HRMS calcd for $C_{39}H_{30}N_6$: 582.2532. Found: 582.2528.

Synthesis of DPA-C G1 Dendron. Benzophenone (8.59 g, 47.1 mmol), 4,4′-diaminobenzophenone (1.00 g, 4.71 mmol), and 1,4-diazabiclo[2.2.2]octane (DABCO) (1.06 g, 9.42 mmol) were dissolved in chlorobenzene (100 mL). Titanium(IV) tetrachloride (0.45 g, 2.36 mmol) was added in a dropwise manner. The addition funnel was rinsed with chlorobenzene (2 mL). The reaction mixture was heated in an oil bath at 120 °C for 17 h. The precipitate was removed by filtration. The filtrate was concentrated; the DPA-C G1 dendron (0.723 g, 1.91 mmol, 41%) was isolated by silica gel column chromatography (ethyl acetate:dichloromethane:hexane = 1:1:6−1:1:3, R_f = 0.54 in the solution of ethyl acetate:dichloromethane:hexane = 1:1: 1). DPA-C G1 dendron: ^{1}H NMR (400 MHz, CDCl$_3$, TMS): δ = 7.76 (d, J = 7.2 Hz, 2H), 7.62 (d, J = 8.4 Hz, 2H), 7.59 (d, J = 8.4 Hz, 2H), 7.48 (t, J = 7.2 Hz, 1H), 7.41 (dd, J = 7.2, 7.2 Hz, 2H), 7.27 (br, 3H), 7.13 (br, 2H), 6.78 (d, J = 8.4 Hz, 2H), 6.61 (d, J = 8.4 Hz, 2H), 4.17 (s, 2H). ^{13}C NMR (100 MHz, CDCl$_3$, TMS): δ = 194.35, 168.52, 154.41, 150.49, 138.92, 135.48, 133.08, 132.44, 130.88, 130.56, 129.27, 129.20, 128.75, 128.09, 127.87, 127.52, 120.14, 113.39. IR (KBr, cm^{-1}): 3486 (ν_{as} NH$_2$), 3350 (ν_s NH$_2$), 1645 (ν C=O), 1625 (ν C=N), 1584 (phenyl). MALDI-TOF-MS: 377 [M + H]$^+$. Anal. Calcd for $C_{26}H_{20}N_2O$: C, 82.95; H, 5.35; N, 7.44. Found: C, 82.57, H, 5.41; N, 7.49.

Synthesis of DPA-C G1. The DPA-C G1 dendron (0.500 g, 1.33 mmol) and DABCO (0.448 g, 3.99 mmol) were dissolved in chlorobenzene (60 mL). Titanium(IV) tetrachloride (0.189 g, 0.996 mmol) was added in a dropwise manner. The addition funnel was rinsed with chlorobenzene (2 mL). The reaction mixture was heated in an oil bath at 110 °C for 22 h. The precipitate was removed by filtration. The filtrate was concentrated; DPA-C G1 (0.202 g, 0.188 mmol, 42%) was isolated by silica gel column chromatography (ethyl acetate:dichloromethane:hexane = 1:1:5, R_f = 0.60 in the solution of ethyl acetate:dichloromethane:hexane = 1:2:3). DPA-C G1: ^{1}H NMR (400 MHz, CDCl$_3$, TMS): δ = 7.74 (d, J = 7.2 Hz, 6H), 7.64 (d, J = 8.4 Hz, 6H), 7.48 (t, J = 7.2 Hz, 3H), 7.40 (dd, J = 7.2, 7.2 Hz, 6H), 7.30 (m, 9H), 7.14 (dd, J = 7.2, 1.6 Hz, 6H), 6.75 (d, J = 8.4 Hz, 6H), 6.69 (d, J = 8.4 Hz, 6H), 6.44 (d, J = 8.4 Hz, 6H). ^{13}C NMR (100 MHz, CDCl$_3$, TMS): δ = 170.58, 168.31, 153.92, 152.56, 139.20, 135.71, 132.93, 130.83, 130.65, 129.68, 129.33, 128.74, 128.12, 127.98, 120.55, 119.59. IR (KBr, cm^{-1}): 1617 (ν C=N), 1587 (phenyl). MALDI-TOF-MS: 1076 [M + H]$^+$. Anal. Calcd for $C_{78}H_{54}N_6$: C, 87.12; H, 5.06; N, 7.82. Found: C, 86.93, H, 5.17; N, 7.71.

Synthesis of DPA-C G2 Dendron. The DPA G2 dendron[8] (11.3 g, 20.9 mmol), 4,4′-diaminobenzophenone (0.892 g, 4.20 mmol), and DABCO (1.41 g, 12.6 mmol) were dissolved in chlorobenzene (300 mL). Titanium(IV) tetrachloride (0.398 g, 2.10 mmol) was added dropwisely. The addition funnel was rinsed with chlorobenzene (2 mL). The reaction mixture was heated in an oil bath at 120 °C for 21 h. The precipitate was removed by filtration. The filtrate was concentrated; the DPA-C G2 dendron (1.11 g, 1.51 mmol, 36%) was isolated by silica gel column chromatography (ethyl acetate:dichloromethane:hexane = 1:2:5−1:2:4, R_f = 0.59 in solution of ethyl acetate:dichloromethane:hexane = 1:1:1). DPA-C G2 dendron: ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 7.76 (d, J = 7.2 Hz, 2H), 7.72 (d, J = 7.2 Hz, 2H), 7.67 (d, J = 8.4 Hz, 2H), 7.56 (d, J = 8.4 Hz, 2H), 7.54 (d, J = 8.4 Hz, 2H), 7.47−7.35 (m, 6H), 7.29 (br, 3H), 7.16 (br, 5H), 6.99 (br, 2H), 6.86 (d, J = 8.4 Hz, 2H), 6.76 (d, J = 8.4 Hz, 2H), 6.67 (d, J = 8.4 Hz, 2H), 6.65 (d, J = 8.4 Hz, 2H), 6.57 (d, J = 8.4 Hz, 2H), 4.17 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 194.20, 168.78, 168.26, 168.12, 154.78, 153.66, 151.74, 150.47, 138.97, 138.79, 135.55, 135.31, 133.78, 132.54, 132.34, 130.74, 130.54, 130.17, 129.95, 129.86, 129.18, 129.11, 129.01, 128.64, 128.58, 127.99, 127.84, 127.65, 127.53, 120.40, 120.36, 120.08, 113.36. IR (KBr, cm^{-1}): 3449 (ν_{as} NH_2), 3389 (ν_s NH_2), 1644 (ν C=O), 1623 (ν C=N), 1579 (phenyl). FAB-MS: 735 [M + H]$^+$. Anal. Calcd for $C_{52}H_{38}N_4O$: C, 84.99; H, 5.21; N, 7.62; Found: C, 85.20, H, 5.42; N, 7.50.

Synthesis of DPA-C G2. The DPA-C G2 dendron (0.721 g, 0.982 mmol) and DABCO (0.331 g, 2.95 mmol) were dissolved in chlorobenzene (50 mL). Titanium(IV) tetrachloride (0.140 g, 0.736 mmol) was added in a dropwise manner. The additional funnel was rinsed with chlorobenzene (2 mL). The reaction mixture was heated in an oil bath at 110 °C for 19 h. The precipitate was removed by filtration. The filtrate was concentrated; DPA-C G2 (0.495 g, 0.230 mmol, 70%) was isolated by silica gel column chromatography (ethyl acetate: dichloromethane:hexane = 1:1:4, R_f = 0.68 in the solution of ethyl acetate:dichloromethane:hexane = 1:2:2). DPA-C G2: ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 7.75 (d, J = 7.2 Hz, 6H), 7.73 (d, J = 7.2 Hz, 6H), 7.64 (d, J = 8.0 Hz, 6H), 7.50 (d, J = 8.0 Hz, 6H), 7.48−7.35 (m, 18H), 7.29 (m, 9H), 7.25 (t, J = 7.2 Hz, 3H), 7.19 (dd, J = 7.2, 7.2 Hz, 6H), 7.14 (d, J = 7.2 Hz, 6H), 7.01, (d, J = 7.2 Hz, 6H), 6.87 (d, J = 8.0 Hz, 6H), 6.80 (d, J = 8.0 Hz, 6H), 6.73 (d, J = 8.0 Hz, 6H), 6.65 (d, J = 8.0 Hz, 6H), 6.58 (d, J = 8.0 Hz, 6H), 6.55 (d, J = 8.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 170.45, 168.83, 168.33, 168.00, 154.24, 153.63, 152.71, 151.77, 139.12, 138.93, 135.66, 135.46, 134.10, 132.46, 130.82, 130.67, 130.43, 130.00, 129.60, 129.28, 128.72, 128.68, 128.10, 127.92, 127.71, 120.92, 120.44, 120.19, 119.63. IR (KBr, cm^{-1}): 1617 (ν C=N), 1578 (phenyl). MALDI-TOF-MS: 2151 [M + H]$^+$. Anal. Calcd for $C_{156}H_{108}N_{12}$: C, 87.12; H, 5.06; N, 7.82. Found: C, 87.22, H, 5.12; N, 7.77.

Synthesis of DPA-C G3 Dendron. The DPA G3 dendron[8] (6.11 g, 4.86 mmol), 4,4′-diaminobenzophenone (0.206 g, 0.971 mmol), and DABCO (0.490 g, 4.37 mmol) were dissolved in chlorobenzene (100 mL). Titanium(IV) tetrachloride (0.138 g, 0.728 mmol) was added in a dropwise manner. The addition funnel was rinsed with chlorobenzene (2 mL). The reaction mixture was heated in an oil bath at 120 °C for 21 h. The precipitate was removed by filtration. The filtrate was concentrated; the DPA-C G3 dendron (0.272 g, 0.187 mmol, 19%) was isolated by silica gel column chromatography (ethyl acetate:dichloromethane:hexane = 1:2:4−1:1:4−1:1:3, R_f = 0.67 in the solution of ethyl acetate:dichloromethane:hexane = 1:1:1). DPA-C dendron G3: ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 7.75−7.69 (m, 8H), 7.62 (d, J = 8.8 Hz, 2H), 7.59 (d, J = 8.8 Hz, 2H), 7.54−7.34 (m, 18H), 7.29 (br, 6H), 7.22 (br, 3H), 7.13 (br, 7H), 7.02 (br, 2H), 7.00 (br, 2H), 6.87 (d, J = 8.0 Hz, 4H), 6.79 (d, J = 8.4 Hz, 2H) 6.75−6.71 (m, 6H), 6.67 (d, J = 8.4 Hz, 2H), 6.58 (d, J = 8.8 Hz, 2H), 6.58−6.51 (m, 6H), 4.00 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 194.21, 168.88, 168.73, 168.39, 168.19, 168.07, 155.01, 154.26, 153.71, 153.64, 152.00, 151.84, 150.27, 139.18, 138.97, 135.71, 135.53, 134.23, 134.09, 133.58, 132.81, 132.46, 130.88, 130.66, 130.50, 130.34, 130.17, 130.06, 129.89, 129.35, 128.79, 128.69, 128.62, 128.15, 127.97, 127.86, 127.79, 120.85, 120.68, 120.48, 120.25, 119.96, 113.51. IR (KBr, cm^{-1}): 3457 (ν_{as} NH_2), 3388 (ν_s NH_2), 1642 (ν C=O), 1617 (ν C=N), 1578 (phenyl). MALDI-TOF-MS: 1452 [M + H]$^+$.

Synthesis of DPA-C G3. The DPA-C G3 dendron (0.272 g, 0.187 mmol) and DABCO (0.246 g, 2.19 mmol) were dissolved in chlorobenzene (30 mL). Titanium(IV) tetrachloride (0.104 g, 0.547 mmol) was added in a dropwise manner. The addition funnel was rinsed with chlorobenzene (2 mL). The reaction mixture was heated in an oil bath at 110 °C for 22 h. The precipitate was removed by filtration. The filtrate was concentrated; the DPA-C G3 (0.264 g, 0.0614 mmol, 99%) was isolated (R_f = 0.64 in the solution of ethyl acetate:dichloromethane:hexane = 1:2:2). DPA-C G3: ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 7.74−6.31 (m, 216H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 170.10, 168.67, 168.51, 168.19, 167.97, 167.85, 154.02, 153.49, 152.25, 152.03, 151.67, 151.48, 138.97, 138.80, 138.64, 135.52, 134.20, 133.90, 133.46, 132.62, 132.13, 130.69, 130.29, 130.15, 129.88, 129.45, 129.15, 128.59, 127.95, 127.79, 127.61, 120.96, 120.68, 120.30, 120.05, 119.82, 119.36. IR (KBr, cm^{-1}): 1615 (ν C=N), 1578 (phenyl). MALDI-TOF-MS: 4302 [M + H]$^+$. Anal. Calcd for $C_{312}H_{216}N_{24}$: C, 87.12; H, 5.06; N, 7.82. Found: C, 86.95, H, 5.25; N, 7.64.

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Supporting Information Available: X-ray crystallographic data file (CIF) for CPA-3a. This material is available free of charge via the Internet at http://pubs.acs.org.

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