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First Synthesis of Phenylazomethine Dendrimer Ligands and Structural Studies

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Abstract: Novel dendritic polyphenylazomethines (DPAs), which consist of a π-conjugated backbone, were synthesized up to the fourth generation by the convergent method via dehydration of aromatic ketones with aromatic amines in the presence of titanium(IV) tetrachloride. The obtained dendrimers, DPA G1−4 (designated as G*X*, where *X* is the generation number), show high thermostability ($\mathrm{Td}_{10\%}$ 521 °C in DPA G4) and high solubility for the common solvents such as chloroform, THF, and DMSO unlike the conventional linear polyphenylazomethines, which have very low solubilities. The DPA G4 molecule was confirmed to have a spherelike structure by GPC measurement and a molecular model based on the crystal structure of DPA G2. Crystal data for DPA G2: monoclinic space group $P2_1/a$, $a = 25.352(4)$ Å, $b = 8.577(2)$ Å, $c = 16.151(2)$ Å, $\beta = 106.25(1)°$, $V = 3371.6(10)$ Å^3, $Z = 2$, $D_{\mathrm{calc}} = 1.168$ g/cm^3, $\mu(\mathrm{Cu\ K}\alpha) = 0.536$ cm^{-1}, final $R = 0.089$, and $R_{\mathrm{w}} = 0.287$. The molecular modeling reveals that a DPA G4 molecule has a spherelike structure, in which the height, width, and depth are 2.3, 2.9, and 2.5 nm, respectively. The TEM and AFM pictures show the DPA G4 molecules to have a spherelike structure (the diameter: 2.3 nm) and are regularly assembled on a plate by casting. The occupied area of one DPA G4 molecule in a monolayer on water was estimated by $\pi-A$ measurements to be 3.8−4.2 nm^2 (the calculated diameter 2.2−2.3 nm, which agreed with the TEM result). NMR studies (^{1}H NMR at 130 °C and T_1 measurements) supported a conformational rigidity of DPA G4 in solution.

Introduction

Dendrimers are perfectly branched polymers with a beautiful spherelike shape.[1] Therefore, dendrimers can possibly be regularly assembled with a packing structure on a plate. However, most dendrimers, which consist of a single-bond backbone, are too soft and easily deformed to form a three-dimensionally packing structure on a plate.[2] In this respect, rigid dendrimers, especially dendrimers with a π-conjugated backbone, are expected to expand the field of nanomarerials, and some types of rigid dendrimers have been reported.[3] Linear polyphenylazomethines are known as π-conjugated polymers with high thermostability,[4] but their very poor solubility prevents structural studies or practical applications as polymer materials. However, the high thermostability, the rigidity based on the π-conjugated backbone, and the high coordination ability of the imine nitrogen are very attractive as a nanomaterial for electronic or photoelectronic devices. We now report the first synthesis of dendritic polyphenylazomethines (DPAs)[5] via the convergent method and reveal that the DPA molecules have a spherelike structure with a conformational rigidity based on various measurements such as GPC, molecular modeling using crystal data, NMR, TEM, AFM, and $\pi-A$ measurements. The novel dendrimers are expected to be nanosized sphere ligands with various metal ions such as Ag, Sn, and Eu,[6] which forms a three-dimensionally packed structure.

Results and Discussion

Convergent Synthesis of Dendritic Polyphenylazomethines. Novel dendritic polyphenylazomethines (DPA G1, G2, G3, and G4, designated as G*X*, where *X* is the generation number)

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(1) See the following reviews about dendrimers: (a) Tomalia, D. A.; Naylor, A. M.; Goddard, W. A., III. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 138. (b) Bosman, A. W.; Janssen H. M.; Meijer, E. W. *Chem. Rev.* **1999**, *99*, 1665. (c) Fischer, M.; Vögtle, F. *Angew. Chem., Int. Ed.* **1999**, *38*, 884.

(2) (a) Hierlemann, A.; Campbell, J. K.; Baker, L. A.; Crooks, R. M.; Ricco, A. J. *J. Am. Chem. Soc.* **1998**, *120*, 5323. (b) Tokuhisa, H.; Zhao, M.; Baker, L. A.; Phan, V. T.; Dermody, D. L.; Garcia, M. E.; Peez, R. F.; Crooks, R. M.; Mayer, T. M. *J. Am. Chem. Soc.* **1998**, *120*, 4492. (c) Li, J.; Swanson, D. R.; Qin, D.; Brothers, H. M.; Piehler, L. T.; Tomalia, D.; Meier, D. J. *Langmuir* **1999**, *15*, 7347.

(3) For reported dendrimers with a π-conjugated backbone, see the following: *Polyphenylene dendrimers*. (a) Berresheim, A. J.; Müller, M.; Müllen, K. *Chem. Rev.* **1999**, *99*, 1747. (b) Morgenroth, F.; Reuther, E.; Müllen, K. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 631. *Phenylacetylene dendrimers*. (c) Moore, J. S. *Acc. Chem. Res.* **1997**, *30*, 402. (d) Devadoss, C.; Bharathi, P.; Moore, J. S. *J. Am. Chem. Soc.* **1996**, *118*, 9635. *Stilbenoid dendrimers*. (e) Meier, H.; Lehmann, M. *Angew. Chem., Int. Ed.* **1998**, *37*, 643. (f) Deb, S. K.; Maddux, T. M.; Yu, L. *J. Am. Chem. Soc.* **1997**, *119*, 9079. *Dendritic nanorod*. (g) Stocker, W.; Karakaya, B.; Schürmann, B. L.; Rabe, J. P.; Schlüter, A. D. *J. Am. Chem. Soc.* **1998**, *120*, 7691. (h) Bo, Z.; Rabe, J. P.; Schlüter, A. D. *Angew. Chem., Int. Ed.* **1999**, *38*, 2370. (i) Schlüter, A. D.; Rabe, J. P. *Angew. Chem., Int. Ed.* **2000**, *39*, 864.

(4) (a) Volpe, A. A.; Carson Jr., J. C.; Kaufman, L. G. *Thermochim. Acta* **1971**, *2*, 175. (b) Kaufman, L. G.; Funke, P. T.; Volpe, A. A. *Polym. Prepr. (Am. Chem. Soc. Div. Polym. Chem.)* **1970**, *11*, 250.

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(6) For reported dendrimer−metal complexes, see the following: (a) Petrucci-Samija, M.; Guillemette, V.; Dasgupta, M.; Kakkar, A. K. *J. Am. Chem. Soc.* **1999**, *121*, 1968. (b) Balogh, L.; Tomalia, D. A. *J. Am. Chem. Soc.* **1998**, *120*, 7355. (c) Zhao, M.; Sun, L.; Crooks, R. M. *J. Am. Chem. Soc.* **1998**, *120*, 4877.

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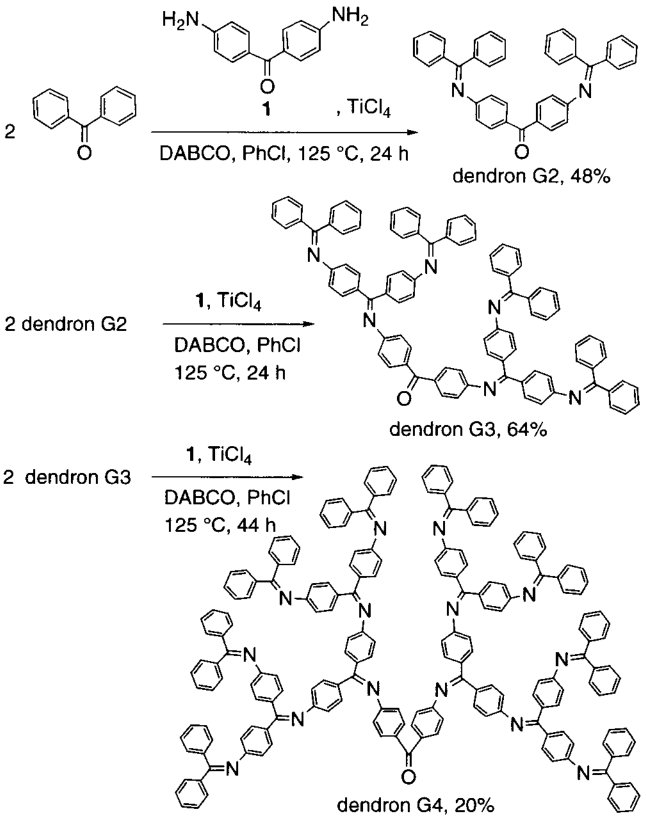
Scheme 1. Convergent Synthesis of the DPA Dendrons



were synthesized by the convergent method as shown in Schemes 1 and 2. Benzophenone was allowed to react with 4,4′-diaminobenzophenone (**1**) in the presence of titanium(IV) tetrachloride and 1,4-diazabicyclo[2.2.2]octane (DABCO). Titanium(IV) tetrachloride is a more effective agent for the dehydration of aromatic ketones with aromatic amines than *p*-toluenesulfonic acid (PTS), which is a common dehydration agent.[7] In addition, PTS is not suitable in such multistep syntheses for dendrimer preparation, because the ready-formed azomethine bonds can possibility be hydrolyzed due to the equilibrium reaction. On the other hand, titanium(IV) tetrachloride is a good agent for this synthesis, since the dehydration using titanium(IV) tetrachloride is irreversible. The DPA dendron G2 was synthesized via the dehydration reaction and isolated by silica gel column chromatography with a 48% yield. An undesirable dehydration between two molecules of **1** lowered the yield of the dendron.[8] DPA dendrons G3 and G4 were obtained in 64 and 20% yields by dehydration of the dendrons G2 and G3 with **1**, respectively. DPAs G1, G2, G3, and G4 were obtained by dehydration of benzophenone, the dendrons G2, G3, and G4 with *p*-phenylenediamine, and isolated in 91, 62, 45, and 31% yields, respectively. The isolated dendrons and dendrimers were identified by MS, NMR, IR, and elemental analysis. GPC analysis ($M_w/M_n = 1.02$) and the MALDI-TOF-MS spectrum of DPA G4 are shown in Figure 1. The concentration of Ti in the DPA G4 powder was confirmed by ICP-MS to be under 0.1 ppm.

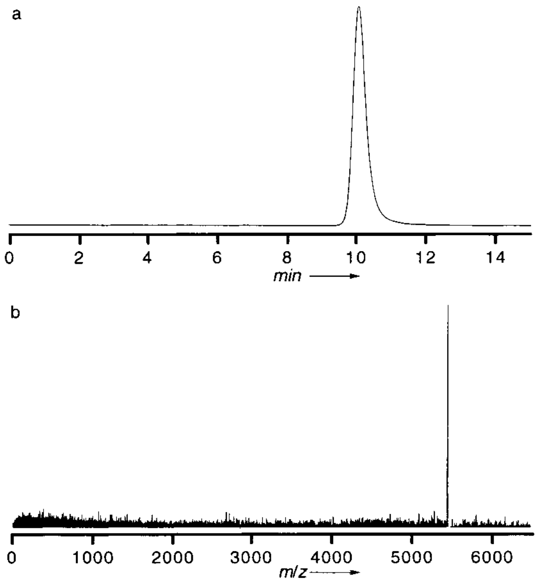
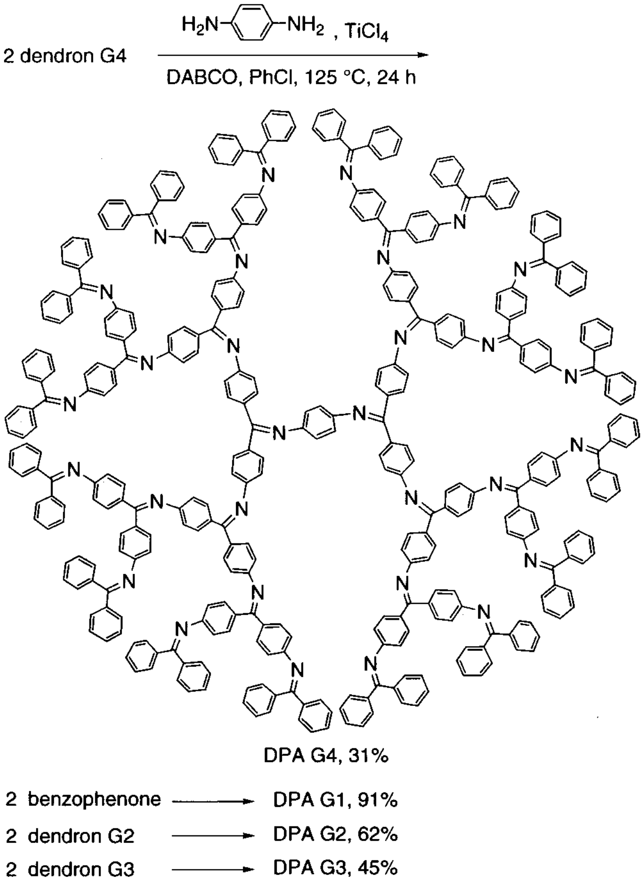


Figure 1. (a) GPC trace of DPA G4 ($M_w/M_n = 1.02$). (b) MALDI-TOF-MS spectrum of DPA G4 (calcd 5451.26 $[M + H]^+$, found 5451.48).

Scheme 2. Synthesis of DPAs (DPA G1−4)



Solubility and Thermostability. Conventional linear polyphenylazomethines have very poor solubility; therefore, a structural study is difficult. On the other hand, the obtained DPAs showed high solubility for common solvents such as chloroform, THF, or DMSO. Weak π-stacking between the DPA molecules due to the conformational bulkiness is considered to enhance the solubility. The high solubility enabled the structural studies and the molecular assembling on a plate as will be described later. Moreover, DPAs showed a high thermostability

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[7] (a) Trost, B. M., Fleming, I., Eds. *Comprehensive Organic Synthesis*; Pergamon Press: New York, 1991; Vol. 6, p 705. (b) Higuchi, M.; Yamamoto, K. *Org. Lett.* **1999**, *1*, 1881. (c) Higuchi, M.; Kimoto, A.; Shiki, S.; Yamamoto, K. *J. Org. Chem.* **2000**, *65*, 5680.

[8] The dendron G2 is easily separated from the side product arising by dehydration of two molecules of **1** by silica gel column chromatography, because the polarity of the side product, which has amino groups, is higher than that of the dendron, which has no amino groups.

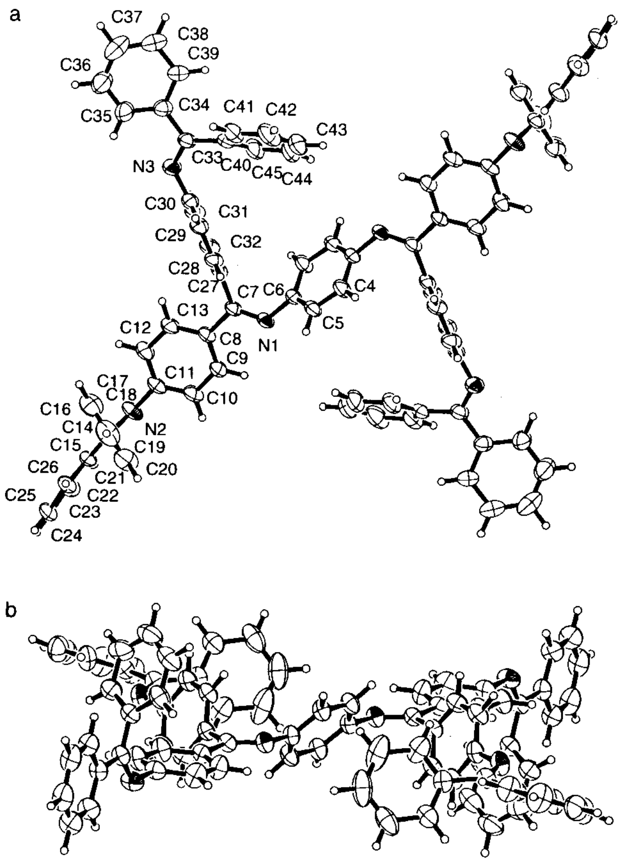

Figure 2. ORTEP drawing of DPA G2 with 30% ellipsoid. (a) Top view; (b) Side view. Selected dihedral angles: N1−C7−C8−C9, −7.2(5)°; N1−C7−C27−C28, 117.3(4)°; C4−C6−N1−C7, 51.7(5)°; N2−C14−C21−C26, −3.6(6)°; N2−C14−C15−C16, 75.4(5)°; C12−C11−N2−C14, −88.0(5)°; N3−C33−C34−C35, 26.4(6)°; N3−C33−C40−C45, 50.5(6)°; C31−C30−N3−C33, 64.8(5)°.

similar to the linear polymer. The temperatures for a 10% weight loss ($Td_{10\%}$) of DPAs G2, -3, and -4 were determined by thermogravimetric analysis to be 514, 511, and 521 °C, respectively, while that of the linear polymer was 507 °C.[7c] The dendrimers and the linear one have similar thermostabilities, although the dendrimers have many terminals, which are easy to evaporate by thermal cleavage. The strong imine bond, which has a large bond energy (615 kJ/mol), is considered to cause the high thermostability.

X-ray Structural Analysis and Molecular Modeling. Characterization by single-crystal X-ray diffraction provides correct information about the structure of the dendrimers in the solid state. X-ray crystals of DPA G2 were obtained by slow vapor diffusion of methanol into a chlorobenzene solution of DPA G2. The molecular structure of DPA G2 is illustrated in Figure 2. Crystal data and data collection parameters are presented in the Experimental Section and Supporting Information (CIF format). The results reveal that DPA G2 has a centrosymmetrical and two-dimensionally expanded structure.

Molecular modeling of DPA G4 was performed based on the following three facts obtained from the crystal structure of DPA G2. (1) The dendrimer is centrosymmetrical in the crystals. (2) There exists a conformational pattern among the three phenyl rings connected to the imine bonds as follows. Phenyl rings connected to the imine nitrogens of DPA G2 (N-connected phenyl rings) are perpendicular to the imine bond (C12−C11−N2−C14 angle, −88.0(5)°), and the angle is twisted about 30−40° by steric hindrance (C31−C30−N3−C33 angle, 64.8(5)°; C4−C6−N1−C7 angle, 51.7(5)°). In the two phenyl rings connected to the imine carbons (C-connected phenyl rings), the trans ones for the N-connected phenyl ring are parallel to the imine bond (N1−C7−C8−C9 angle, −7.2(5)°; N2−C14−C21−C26 angle, −3.6(6)°), and the angle is twisted ~30° by steric hindrance (N3−C33−C34−C35 angle, 26.4(6)°). On the other hand, the cis C-connected phenyl rings are rather perpendicular to the imine bond (N1−C7−C27−C28 angle, 117.3(4)°; N2−C14−C15−C16 angle, 75.4(5)°; N3−C33−C40−C45 angle, 50.5(6)°); (3) The cis C-connected phenyl rings at the terminals of the dendritic branch elongate toward the *inside* of the dendrimer.

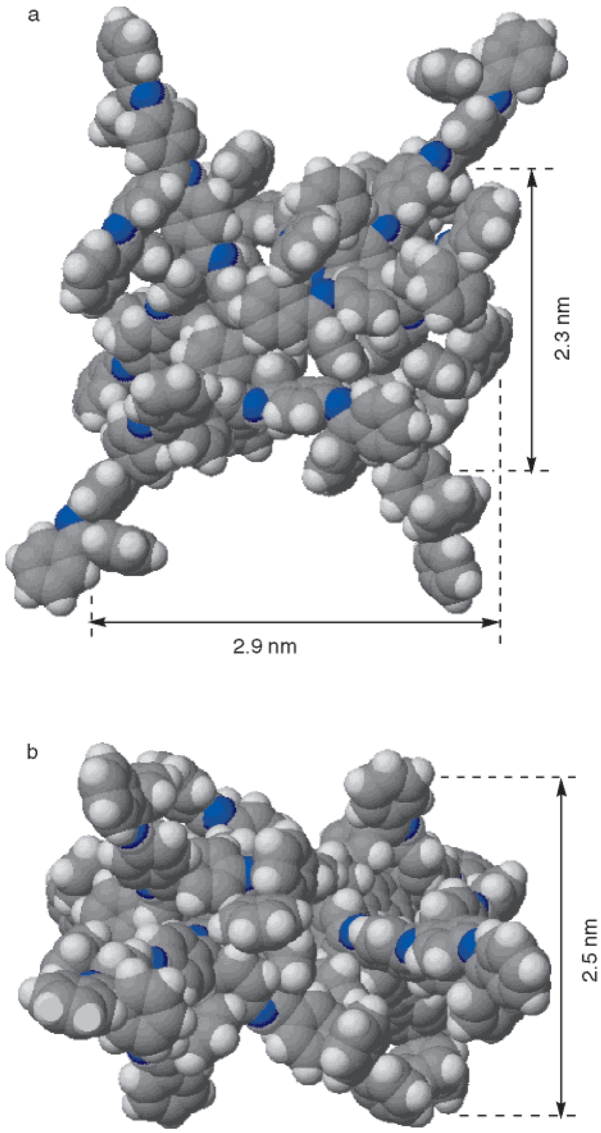

Figure 3. Molecular model of DPA G4 based on the crystal structure of DPA G2.

The molecular model of DPA G4 is shown in Figure 3. With increasing generation, the molecular structure of the dendrimer became three-dimensionally expanded due to the steric hindrance among the branches. As a result, a DPA G4 molecule was postulated to have a spherelike structure (2.5 × 2.9 × 2.3 nm) with four horns in the solid state.[9]

TEM, AFM, and π−A Measurements. The combination of TEM and AFM gives direct information about the molecular

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[9] Molecular dynamics calculation on DPA G4 was also performed and is shown in Supporting Information.

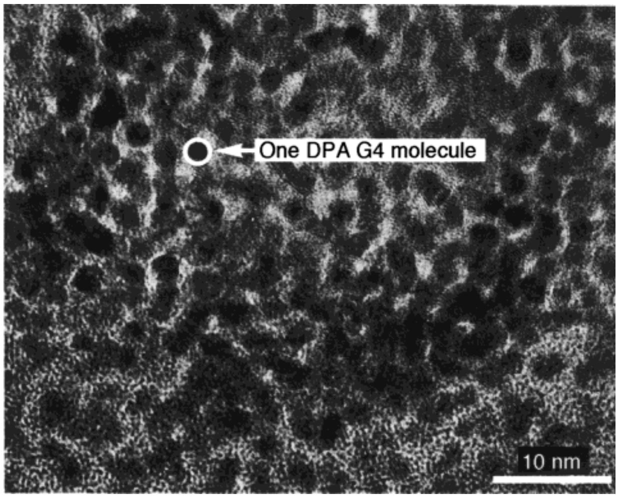

Figure 4. TEM picture of DPA G4.

shape of a dendrimer. In general, the TEM picture of a dendrimer shows the two-dimensionally correct figure of the molecule but gives little information as to the height. On the other hand, the AFM picture of a dendrimer, which is usually taken in the noncontact mode, reveals the height of the dendrimer on a plate. The DPA G4 molecule was confirmed by TEM to have a round shape with a 2.3 ± 0.3 nm diameter (Figure 4). The quality of the picture is not necessarily good because of the high resolution,[10] but we noticed that the diameter of a DPA G4 molecule (2.3 ± 0.3 nm) is much smaller than those of a similar generation of previously reported dendrimers.[11] Reported dendrimers consisting of a single-bond backbone, such as PAMAM, are deformed on a plate; therefore, the diameter observed by TEM is much longer than the height. In other words, the small diameter of a DPA G4 molecule indicates having a three-dimensionally expanded structure without deformation on a plate. The AFM measurement revealed that the DPA G4 molecules are assembled in a multilayered packing structure on a graphite plate by casting (Figure 5a−c). Though the resolution is close to the limit in the tapping mode, a lattice pattern was observed in the picture and the cross section clearly shows alignment of the spherical molecules in a multilayer. The height of the DPA G4 molecule was estimated from the cross section to be at least 2.0 ± 0.1 nm (Figure 5d,e). The observed height will be smaller than the actual height of the dendrimer due to overlap with the underlayer. Anyway, these results revealed that the DPA G4 molecules have a spherelike structure with ~2.3-nm diameter, which almost agreed with that obtained by the molecular modeling. Interestingly, DPA G4 molecules assembled without deformation of the molecule on a plate because of the conformational rigidity.[12]

The occupied area of a DPA molecule in a monolayer on water was estimated by the $\pi-A$ measurement of the DPAs (Figure 6). The $\pi-A$ isotherms of DPA G2−4 showed a transition behavior on pure water. The DPA G4 curve rose with the limiting area of 3.8−4.2 nm^2. The diameter of a DPA G4 molecule was calculated from the area to be 2.2−2.3 nm. This value agrees with that determined by the TEM result.

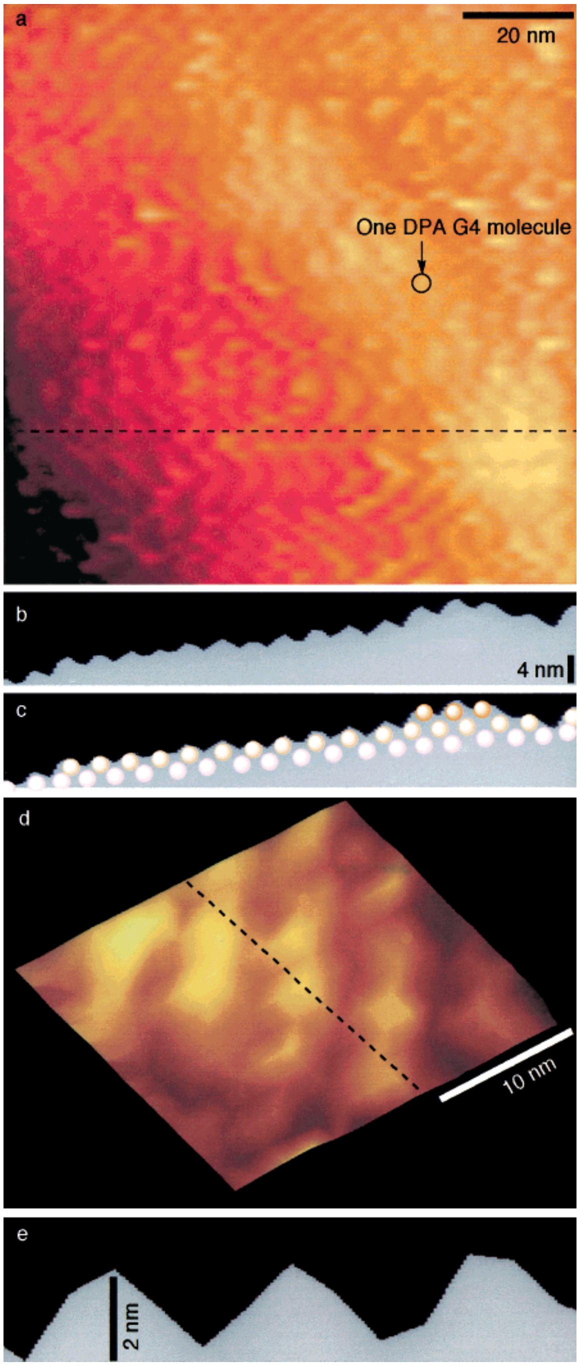

Figure 5. (a) AFM picture of DPA G4 (125 × 125 nm) and (b) cross section at the dotted line of (a). (c) Multilayered structure of DPA G4. (d) AFM picture of DPA G4 (25 × 25 nm) and (e) cross section at the dotted line of 5d.

GPC Analysis. In the gel permeation chromatograph (GPC) analysis, the linear and rigid polymers have a shorter elution time than expected from the molecular weight, while spherelike polymers such as the dendrimers have longer ones.[13] In addition, the M_w/M_n of the dendrimers is close to 1.0 due to the single molecular weight. The M_ns of DPA G1−4, which were calculated using a polystyrene standard in GPC, were 300, 1000,

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[10] The dendrimer shapes are indistinct because the grain of the carbon substrate is closer in size to the dendrimer and the edges become more difficult to delineate.

[11] The diameter of the fifth generation of PAMAM dendrimer is 4.3 nm; see: (a) Jackson, C. L.; Chanzy, H. D.; Booy, F. P.; Drake, B. J.; Tomalia, D. A.; Bauer, B. J.; Amis, E. J. *Macromolecules* **1998**, *31*, 6259. The diameter of the second generation of the modified PAMAM dendrimer is 5 nm; see: (b) Díaz, D. J.; Storrier, G. D.; Bernhard, S.; Takeda, K.; Abruña, H. D. *Langmuir* **1999**, *15*, 7351.

[12] Though the resolution is close to the limit in the tapping mode AFM, the heights of isolated DPA G4 molecules are similar to those of the particles packed with each other. The AFM picture including the individual particles of DPA G4 was added in Supporting Information.

[13] (a) Morikawa, A.; Kakimoto, M.; Imai, Y. *Macromolecules* **1992**, *25*, 3247. (b) Yu, D.; Vladimirov, N.; Fréchet, J. M. J. *Macromolecules* **1999**, *32*, 5186.

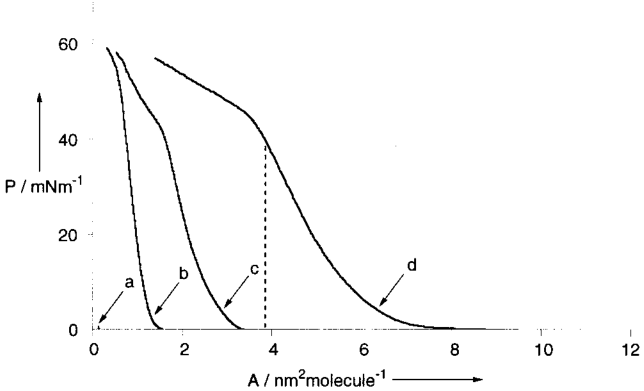

Figure 6. $\pi-A$ measurement of DPAs (G1, line a; G2, line b; G3, line c; G4, line d).

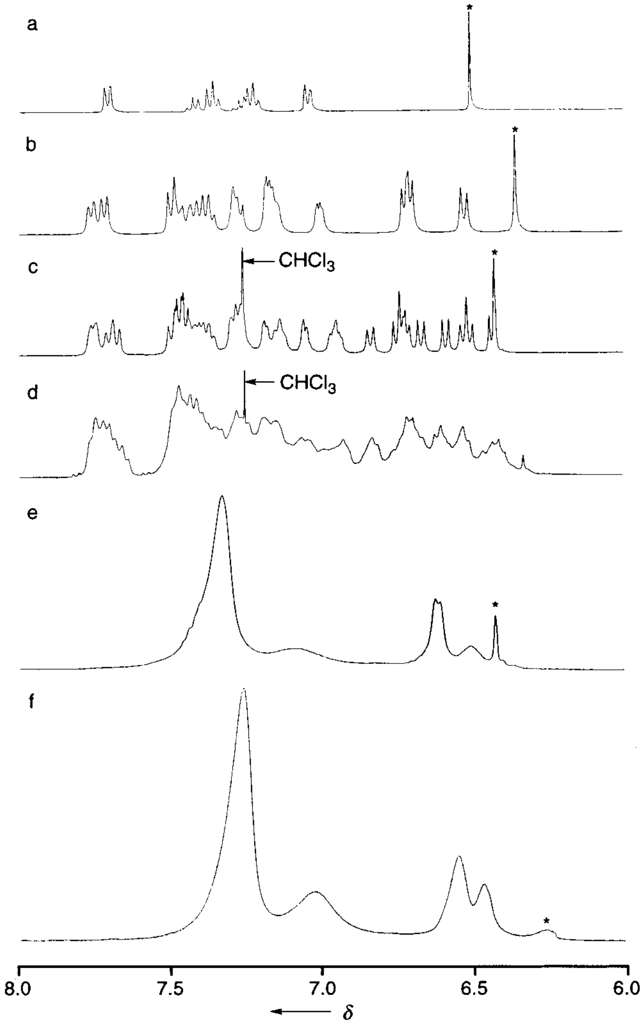

Figure 7. ^{1}H NMR spectra of DPAs (a) G1, (b) G2, (c) G3, and (d) G4 in CDCl$_3$ at 30 °C, and those of DPAs (e) G3 and (f) G4 in DMSO-*d*$_6$ at 130 °C. The marked peaks (*) are attributed to the four protons of the phenyl ring in the core of the DPAs.

2400, and 3800 ($M_w/M_n = 1.02$), respectively, while those determined by FAB- or TOF-MS were 436, 1153, 2587, and 5451, respectively. In DPA G4, the difference between the GPC and TOF-MS results was significant; that is, DPA G4 molecules become close to a compact sphere structure in the solution as well as in the crystal.

NMR Studies. The DPAs have high solubility in common solvents such as chloroform, THF, and DMSO; therefore, structural studies were completed. In each ^{1}H NMR spectrum of DPAs G1, G2, and G3, one singlet peak was observed at 6.6−6.3 ppm, which was attributed by COSY to the four protons of the phenyl ring in the core of the dendrimer (Figure 7a−c). This singlet peak supports the symmetrical structure of the DPAs. On the other hand, a singlet peak was not observed in the spectrum of DPA G4 (Figure 7d). This result shows that the four protons in the core of DPA G4 are not equivalent because of the fixed conformation of the core by the bulky dendrons (Figure 8). However, the broad peak at 6.26 ppm, which was attributed to the four protons of the core, appeared at 130 °C in the DPA G4 spectrum (Figure 7f). This broad peak is based on the slight conformational exchange of the core compared to the sharp peak in the core of DPA G3 at 130 °C (Figure 7e).

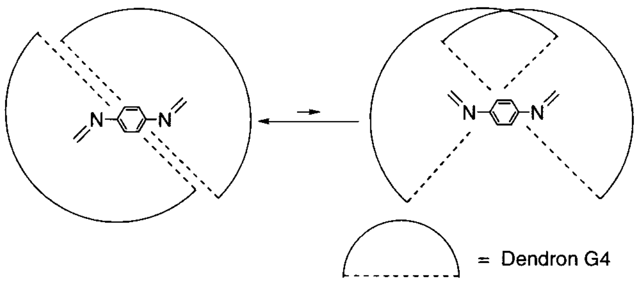

Figure 8. Fixed conformation at the core of DPA G4 by the bulky dendrons.

In Figure 7, the peaks at 7.8−7.6 and 7.45−6.9 ppm are attributed by COSY to the protons of the monosubstituted phenyl rings, i.e., the external phenyl protons of the DPA, while those at 7.6−7.45 and 6.9−6.2 ppm were attributed to the protons of the disubstituted phenyl rings, i.e., the internal phenyl protons. Interestingly, the peaks of the external phenyl protons were broader than those of the internal ones in each dendrimer. To investigate the peak broadening in more detail, we performed spin−lattice (T_1) relaxation measurements of the DPAs. The NMR studies for the relaxation gave useful information about the structural density.[14] With increasing generation, T_1 of the external proton (G1, 1.39 s; G2, 1.44 s; G3, 1.61 s; G4, 2.15 s) increased more than that of the internal one (G1, 1.18 s; G2, 1.23 s; G3, 1.48 s; G4, 1.52 s). The increase in T_1 means a restriction in the molecular motion of the external phenyl rings; therefore, the exterior of DPA G4 is proposed to be close to the solid state.

Conclusion

We first synthesized dendritic polyphenylazomethines up to the fourth generation by the convergent method via dehydration of aromatic ketones with aromatic amines in the presence of titanium(IV) tetrachloride. The obtained dendrimers, which have a single molecular weight, showed a high solubility for common solvents such as chloroform, THF, and DMSO and high thermostability ($Td_{10\%}$ 521 °C in DPA G4). The DPA G4 molecule was postulated to have a spherelike structure (2.3 × 2.9 × 2.5 nm), using a molecular model based on the crystal structure of DPA G2 and GPC measurements. The TEM and AFM picture show that the DPA G4 molecules have a spherelike structure (diameter, 2.3 nm) and are regularly assembled on a plate. An occupied area of a DPA G4 molecule in a monolayer on water was estimated by $\pi-A$ measurements to be 3.8−4.2 nm^{2} (calculated diameter, 2.2−2.3 nm, which agreed with the

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(14) (a) Hecht, S.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1999**, *121*, 4084. (b) Jiang, D.-L.; Aida, T. *Nature* **1997**, *388*, 454. (c) Jansen, J. F. G. A.; de Brabander-van den Berg, E. M. M.; Meijer, E. W. *Science* **1994**, *266*, 1226.

TEM result). The NMR studies revealed a conformational rigidity of the DPA G4 molecules in the solution.

Experimental Section

Synthesis of DPA Dendron G2. Benzophenone (25.7 g, 141 mmol), 4,4′-diaminobenzophenone (3.00 g, 14.1 mmol), and DABCO (9.51 g, 84.8 mmol) were dissolved in chlorobenzene (90 mL). Titanium(IV) tetrachloride (4.02 g, 21.2 mmol) was added dropwise. The addition funnel was rinsed with chlorobenzene (2 mL). The reaction mixture was heated in an oil bath at 125 °C for 24 h. The precipitate was removed by filtration. The filtrate was concentrated; the dendron G2 (3.63 g, 6.71 mmol, 48%) was isolated by silica gel column chromatography (ethyl acetate:hexane = 1:7−1:4, including 1% Et$_3$N, R_f = 0.32 in the solution of ethyl acetate:hexane = 1:5). DPA dendron G2: ^{1}H NMR (400 MHz, CDCl$_3$, 30 °C, TMS) δ 7.76 (br, 4H), 7.57 (d, J = 8.4 Hz, 4H), 7.46 (br, 2H), 7.40 (br, 4H), 7.26 (br, 6H), 7.12 (br, 4H), 6.76 (d, J = 8.4 Hz, 4H); ^{13}C NMR (100 MHz, CDCl$_3$, 30 °C, TMS) δ 195.02, 168.67, 155.11, 139.00, 135.62, 132.53, 131.03, 130.92, 129.40, 129.27, 128.88, 128.20, 127.99, 120.27; IR (KBr, cm^{-1}) 1647 (C═O), 1618 (C═N), 1581 (phenyl), 848, 781, 697; EI-MS 540 [M]$^+$. Anal. Calcd for C$_{39}$H$_{28}$N$_2$O: C, 86.64; H, 5.22; N, 5.18. Found: C, 86.87, H, 4.92; N, 5.09.

Synthesis of DPA Dendron G3. The dendron G2 (4.85 g, 8.97 mmol), 4,4′-diaminobenzophenone (380 mg, 1.79 mmol), and DABCO (1.21 g, 10.8 mmol) were dissolved in chlorobenzene (40 mL). Titanium(IV) tetrachloride (510 mg, 2.69 mmol) was added dropwise. The addition funnel was rinsed with chlorobenzene (2 mL). The reaction mixture was heated in an oil bath at 125 °C for 24 h. The precipitate was removed by filtration. The filtrate was concentrated; the dendron G3 (1.43 g, 1.14 mmol, 64%) was isolated by silica gel column chromatography (ethyl acetate:hexane = 1:5−1:3, including 1% Et$_3$N, R_f = 0.24 in solution of ethyl acetate:hexane = 1:4). DPA dendron G3: ^{1}H NMR (400 MHz, CDCl$_3$, 30 °C, TMS) δ 7.77−7.66 (m, 8H), 7.58 (d, J = 8.4 Hz, 4H), 7.53 (d, J = 8.0 Hz, 4H), 7.49−7.32 (m, 12H), 7.29 (br, 6H), 7.14 (br, 10H), 6.98 (br, 4H), 6.86 (d, J = 7.6 Hz, 4H), 6.74 (d, J = 8.0 Hz, 4H), 6.69 (d, J = 8.4 Hz, 4H), 6.56 (d, J = 7.6 Hz, 4H); ^{13}C NMR (100 MHz, CDCl$_3$, 30 °C, TMS) δ 194.89, 169.00, 168.48, 155.57, 153.98, 152.06, 139.25, 139.07, 135.85, 135.60, 133.97, 132.22, 130.95, 130.16, 130.05, 129.37, 128.80, 128.17, 128.02, 127.84, 120.68, 120.53, 120.28; IR (KBr, cm^{-1}) 1647 (C═O), 1617 (C═N), 1581 (phenyl), 848, 781, 697; FAB-MS 1257 [M + 1]$^+$. Anal. Calcd for C$_{91}$H$_{64}$N$_6$O: C, 86.91; H, 5.13; N, 6.68. Found: C, 86.59, H, 4.79; N, 6.51.

Synthesis of DPA Dendron G4. Dendron G3 (9.52 g, 7.57 mmol), 4,4′-diaminobenzophenone (268 mg, 1.26 mmol), and DABCO (849 mg, 7.57 mmol) were dissolved in chlorobenzene (120 mL). Titanium(IV) tetrachloride (358 mg, 1.89 mmol) was added dropwise. The addition funnel was rinsed with chlorobenzene (2 mL). The reaction mixture was heated in an oil bath at 125 °C for 44 h. The precipitate was removed by filtration. The filtrate was concentrated; the dendron G4 (668 mg, 0.248 mmol, 20%) was isolated by silica gel column chromatography (ethyl acetate:hexane:dichloromethane = 1:6:6−1:3:3, R_f = 0.377 in the solution of ethyl acetate:hexane:dichloromethane = 1:5:5). DPA dendron G4: ^{1}H NMR (400 MHz, CDCl$_3$, 30 °C, TMS) δ 7.74−6.35 (m, 136H); ^{13}C NMR (100 MHz, CDCl$_3$, 30 °C, TMS) δ 194.68, 168.87, 168.43, 168.23, 168.12, 155.46, 154.39, 153.78, 152.07, 139.28, 139.05, 135.83, 134.24, 133.66, 132.36, 130.90, 130.60, 130.21, 130.08, 129.98, 129.36, 128.80, 128.17, 128.01, 127.83, 120.89, 120.74, 120.50, 120.28, 120.04; IR (KBr, cm^{-1}) 1647 (C═O), 1617 (C═N), 1578 (phenyl), 848, 784, 695; MALDI-TOF-MS calcd 2690.11 [M + H]$^+$, found 2690.36. Anal. Calcd for C$_{195}$H$_{136}$N$_{14}$O: C, 87.03; H, 5.09; N, 7.29. Found: C, 87.11, H, 5.24; N, 6.89.

Synthesis of DPA G1. Benzophenone (1.69 g, 9.25 mmol), *p*-phenylenediamine (500 mg, 4.62 mmol), and DABCO (3.11 g, 27.7 mmol) were dissolved in chlorobenzene (40 mL). Titanium(IV) tetrachloride (1.32 g, 6.93 mmol) was added dropwise. The addition funnel was rinsed with chlorobenzene (2 mL). The reaction mixture was heated in an oil bath at 125 °C for 24 h. The precipitate was removed by filtration. The filtrate was concentrated; DPA G1 (1.83 g, 4.19 mmol, 91%) was isolated by silica gel column chromatography (ethyl acetate:hexane = 1:10, R_f = 0.4). DPA G1: ^{1}H NMR (400 MHz, CDCl$_3$, 30 °C, TMS) δ 7.70 (d, J = 7.6 Hz, 4H), 7.44 (t, J = 7.6 Hz, 2H), 7.37 (dd, J = 7.6, 7.6 Hz, 4H), 7.28 (t, J = 7.6 Hz, 2H), 7.23 (dd, J = 7.6, 7.6 Hz, 4H), 7.05 (d, J = 7.6 Hz, 4H), 6.51 (s, 4H); ^{13}C NMR (100 MHz, CDCl$_3$, 30 °C, TMS) δ 167.97, 146.83, 139.74, 136.28, 130.47, 129.47, 129.14, 128.34, 128.06, 127.84, 121.33; IR (KBr, cm^{-1}) 1618 (C═N), 1596 (phenyl), 840, 781, 697; EI-MS 436 [M]$^+$. Anal. Calcd for C$_{33}$H$_{24}$N$_2$: C, 88.04; H, 5.54; N, 6.42. Found: C, 88.19, H, 5.35; N, 6.40.

Synthesis of DPA G2. The dendron G2 (1.00 g, 1.85 mmol), *p*-phenylenediamine (100 mg, 0.925 mmol), and DABCO (623 mg, 5.55 mmol) were dissolved in chlorobenzene (30 mL). Titanium(IV) tetrachloride (264 mg, 1.39 mmol) was added dropwise. The additional funnel was rinsed with chlorobenzene (2 mL). The reaction mixture was heated in an oil bath at 125 °C for 24 h. The precipitate was removed by filtration. The filtrate was concentrated; DPA G2 (664 mg, 0.576 mmol, 62%) was isolated by silica gel column chromatography (ethyl acetate:hexane = 1:6−1:4, including 1% Et$_3$N, R_f = 0.4 in the solution of ethyl acetate:hexane = 1:4). DPA G2: ^{1}H NMR (400 MHz, CDCl$_3$, 30 °C, TMS) δ 7.76 (d, J = 7.3 Hz, 4H), 7.71 (d, J = 7.3 Hz, 4H), 7.49 (d, J = 8.4 Hz, 4H), 7.46−7.35 (m, 12H), 7.28 (m, 6H), 7.19−7.13 (m, 10H), 7.01 (m, 4H), 6.73 (d, J = 8.4 Hz, 4H), 6.71 (d, J = 8.4 Hz, 4H), 6.54 (d, J = 8.4 Hz, 4H), 6.37 (s, 4H); ^{13}C NMR (100 MHz, CDCl$_3$, 30 °C, TMS) δ 168.74, 168.44, 167.34, 153.42, 151.69, 146.96, 139.45, 139.32, 136.00, 135.80, 135.11, 131.03, 130.85, 130.47, 129.88, 129.49, 129.42, 128.80, 128.19, 128.06, 127.94, 121.71, 120.54, 120.10; IR (KBr, cm^{-1}) 1617 (C═N), 1584 (phenyl), 844, 784, 697; FAB-MS 1153 [M + 1]$^+$. Anal. Calcd for C$_{84}$H$_{60}$N$_6$: C, 87.47; H, 5.24; N, 7.29. Found: C, 87.61, H, 5.16; N, 7.13.

Synthesis of DPA G3. The dendron G3 (600 mg, 0.477 mmol), *p*-phenylenediamine (21.6 mg, 0.200 mmol), and DABCO (135 mg, 1.20 mmol) were dissolved in chlorobenzene (30 mL). Titanium(IV) tetrachloride (56.9 mg, 0.300 mmol) was added dropwise. The addition funnel was rinsed with chlorobenzene (2 mL). The reaction mixture was heated in an oil bath at 125 °C for 24 h. The precipitate was removed by filtration. The filtrate was concentrated; DPA G3 (230 mg, 0.0890 mmol, 45%) was isolated by silica gel column chromatography (ethyl acetate:hexane = 1:5−1:2, including 1% Et$_3$N, R_f = 0.46 in the solution of ethyl acetate:hexane = 1:2). DPA G3: ^{1}H NMR (400 MHz, CDCl$_3$, 30 °C, TMS) δ 7.76−7.63 (m, 16H), 7.50−7.33 (m, 36H), 7.31−7.22 (m, 16H), 7.19−7.11 (m, 12H), 7.06 (br, 4H), 6.95 (br, 8H), 6.84 (d, J = 8.4 Hz, 4H), 6.76−6.71 (m, 12H), 6.67 (d, J = 8.4 Hz, 4H), 6.59 (d, J = 8.4 Hz, 4H), 6.54 (d, J = 8.4 Hz, 4H), 6.51 (d, J = 8.4 Hz, 4H), 6.44 (d, J = 8.4 Hz, 4H), 6.43 (s, 4H); ^{13}C NMR (100 MHz, CDCl$_3$, 30 °C, TMS) δ 169.00, 168.83, 168.51, 168.41, 168.11, 167.17, 153.83, 153.78, 153.68, 152.12, 151.95, 151.87, 147.10, 139.41, 139.26, 139.08, 135.94, 135.81, 135.63, 134.56, 134.48, 134.43, 130.88, 130.78, 130.73, 130.47, 130.30, 130.16, 130.11, 129.98, 129.45, 129.30, 128.86, 128.71, 128.23, 128.08, 127.95, 127.90, 121.86, 120.82, 120.79, 120.51, 120.33, 120.00; IR (KBr, cm^{-1}) 1617 (C═N), 1581 (phenyl), 847, 783, 696; MALDI-TOF-MS calcd 2587.2 [M]$^+$, found 2587.0. Anal. Calcd for C$_{188}$H$_{132}$N$_{14}$: C, 87.28; H, 5.14; N, 7.58. Found: C, 87.43, H, 4.84; N, 7.37.

Synthesis of DPA G4. The dendron G4 (400 mg, 0.149 mmol), *p*-phenylenediamine (8.0 mg, 0.074 mmol), and DABCO (49.8 mg, 0.444 mmol) were dissolved in chlorobenzene (20 mL). Titanium(IV) tetrachloride (21.1 mg, 0.111 mmol) was added dropwise. The addition funnel was rinsed with chlorobenzene (2 mL). The reaction mixture was heated in an oil bath at 125 °C for 24 h. The precipitate was removed by filtration. The filtrate was concentrated; DPA G4 (125 mg, 0.0229 mmol, 31%) was isolated by silica gel column chromatography (ethyl acetate:hexane:dichloromethane = 1:4:4−1:3:3, R_f = 0.45 in solution of ethyl acetate:hexane:dichloromethane = 1:3:3). DPA G4: ^{1}H NMR (400 MHz, CDCl$_3$, 30 °C, TMS) δ 7.80−6.31 (m, 276H); ^{13}C NMR (100 MHz, CDCl$_3$, 30 °C, TMS) δ 169.02, 168.79, 168.47, 168.14, 167.95, 167.78, 166.89, 154.19, 154.04, 153.78, 152.27, 151.97, 151.72, 139.39, 139.18, 139.00, 135.89, 135.70, 134.48, 134.33, 134.17, 130.93, 130.70, 130.35, 130.14, 129.43, 128.86, 128.66, 128.22, 128.07, 127.92, 121.67, 121.05, 120.87, 120.79, 120.52, 120.33, 120.05; IR (KBr, cm^{-1}) 1617 (C═N), 1578 (phenyl), 848, 784, 696; MALDI-TOF-MS calcd 5451.26 [M + H]$^+$, found 5451.48.

Crystal Structure Determination. Crystal data of DPAG2$\cdot$$CH_3OH$, $C_{85}H_{64}N_6O$, $M = 1185.48$, monoclinic, space group $P2_1/a$, $a = 25.352(4)$ Å, $b = 8.577(2)$ Å, and $c = 16.151(2)$ Å, $\beta = 106.25(1)°$, $U = 3371.6(10)$ Å^3, $Z = 2$, $D_{calc} = 1.168$ g/cm^3, $\mu = 0.536$ cm^{-1}, crystal size $0.6 \times 0.3 \times 0.1$ mm^3, 5732 reflections measured, $R = 0.089$, and $R_w = 0.287$. Yellow platelike crystals of DPA G2 were obtained by slow diffusion of methanol vapor into a chlorobenzene solution of DPA G2. A suitable crystal was sealed in a capillary with mother liquor to avoid efflorescence. The intensity data were collected at 298 K on a Rigaku AFC-7R diffractometer with graphite-monochromatized Cu Kα radiation ($\lambda = 1.541\,84$ Å). The structure was solved by direct methods on a Silicon Graphics O^2 workstation with the program system TEXSAN.[15] There exists a positional disorder on the oxygen and carbon atoms in methanol of crystallization. The site occupancy factors of each set of the disordered oxygen and carbon atoms were assumed to be 0.3 and 0.2, respectively. Nonhydrogen atoms (O46, C48, and O47, C49) were treated anisotropically, and hydrogen atoms attached to carbon atoms of DPA G2 were introduced at ideal positions. Refinement was based on F with R_w, against all the 5732 reflections. The R value was 0.089 for the 3180 reflections. Atomic parameters are listed in Supporting Information.

TEM Measurement. The chloroform solution (0.2 mg/mL) of DPA G4 was deposited on carbon-coated copper grids, and the grids were inverted on RuO_4 vapor for 15 min. The TEM image was obtained at 120 kV with a JEOL JEM-2010 at a magnification of 300000×. The image of the dendrimer was enlarged 5 times and printed, then scanned into the computer, and analyzed with TIFF image.

AFM Measurement. The chloroform solution of DPA G4 was cast on the graphite, and the dendrimer was examined using a SII SPA300 instrument under ambient conditions. We used the tapping mode of imaging (DFM). Si probes having a spring constant of ~1.8 N/m (SII SI-DF3-A for DFM) were used at a resonance frequency of ~27 kHz. A 1-μm scanner (SPA300-PZT (FS-1A), 927U92) was used.

***π−A* Measurement.** $\pi - A$ Isotherms were measured using a FSD-300 computer-controlled film balance system (USI System). Water used for the subphase was distilled in an Autostill WG220 (Yamato) and deionized by a Milli-Q Lab (Millipore). A mixture of spectroscopic grade benzene/chloroform (80/20 v/v) was used as the spreading solvent. Compression was started ~10 min after spreading at a rate of 0.2 mm/s (or 20 mm^2/s based on area). The subphase temperature was maintained at 20.0 ± 0.2 °C.

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Supporting Information Available: X-ray crystallographic data file (CIF format) for DPA G2, molecular dynamics calculation on DPA G4, and the AFM picture including the individual particles of DPA G4. This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) TEXSAN. Single-Crystal Structure Analysis Software. Version 1.10. Molecular Structure Corp., 3200 Research Forest Drive, The Woodlands, TX 77381, 1999.