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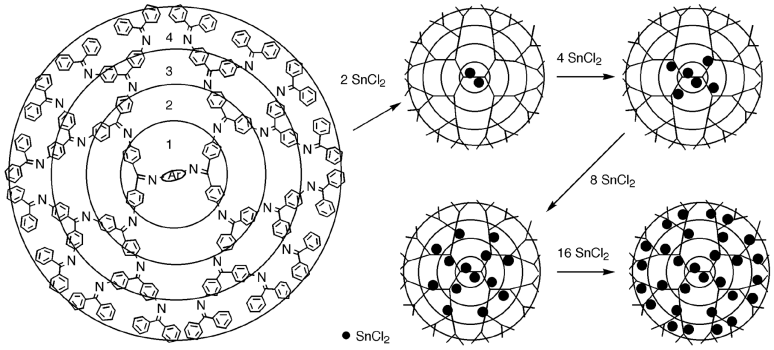

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Control of Stepwise Radial Complexation in Dendritic Polyphenylazomethines

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Abstract: The fourth generation of a dendritic polyphenylazomethine (DPA G4) has 2, 4, 8, and 16 imine groups in the first, second, third, and fourth shells, respectively (total, 30 imine groups). DPA G4 can trap 30 equiv of $SnCl_2$ molecules, because the imine group is complexed with $SnCl_2$ at a ratio of 1:1. During addition of 30 equiv of $SnCl_2$ to DPA G4, four shifts in the isosbestic point were observed in the UV−vis spectra, and the amount of $SnCl_2$ added in each step is in agreement with the number of imine groups in each shell of DPA G4. This result shows that the complexation of the imine groups in DPA G4 with $SnCl_2$ occurs stepwise in the order of the first, second, third, and fourth shells. The unique stepwise complexation was also observed in DPA G2 and G3 as two and three shifts of the isosbestic point, respectively. The stepwise complexation was supported by TEM, NMR, and a novel shell-selective reduction (SSR) method for imines. An expansion in the molecular size of DPA G4 by the complexation was revealed by molecular modeling and TEM measurements. The stepwise complexation is caused by the different basicity of the imine groups between the shells, which was supported by the chemical shifts of the peaks attributed to the imine carbons in the ^{13}C NMR spectra. The gradients in the basicity were controlled by the introduction of electron-withdrawing or -releasing groups to the core of the dendrimers; the core imines were complexed last in DPAs having a 2,3,5,6-tetrafluoro or 2,5-dichlorophenyl core due to the low basicity of the core imines. The different complexation pattern was also clearly confirmed by the SSR method.

Introduction

Organic−metallic hybrid nanomaterials have received much attention for use in electronic, photonic, and magnetic nanodevices. For the further development of these materials, it is essential to control the number and location of metal ions precisely in organic materials. However, in general, metal ions are randomly complexed with the coordination sites of organic polymers. Therefore, the precise control of metal ions is quite difficult. Dendrimers[1] are perfectly branched polymers with successive shells of branch units surrounding a central core. Their tree-like topology causes gradients in the branch density from the interior to the exterior which direct the transfer of charge and energy from the dendrimer periphery to its core.[2] Dendrimers having coordination sites can trap many metal ions or metal clusters within the voids in the dendrimers, which lead to novel organic−metallic hybrid nanomaterials.[3] Dendritic polyphenylazomethines (DPAs) are novel dendritic ligands having many imine groups as coordination sites (Figure 1) and showing high thermal stability and high solubility.[4] We herein report a unique stepwise radial complexation of imine groups in DPAs with $SnCl_2$ based on the gradients in a basicity of the imine groups.[4a] This is the first demonstration of precise control of the number and location of metal ions incorporated into dendritic structures.

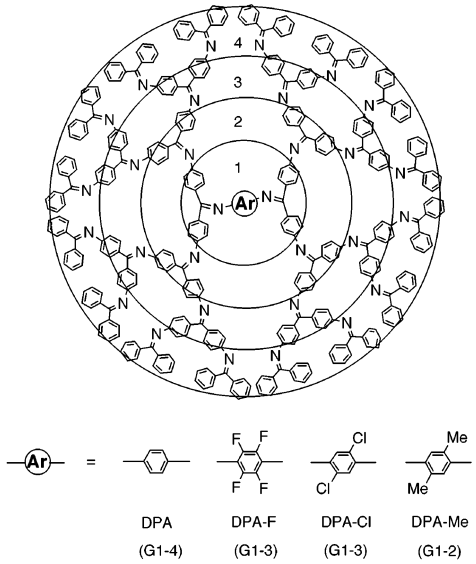

Figure 1. Dendritic polyphenylazomethines (DPA, DPA-F, DPA-Cl, and DPA-Me).

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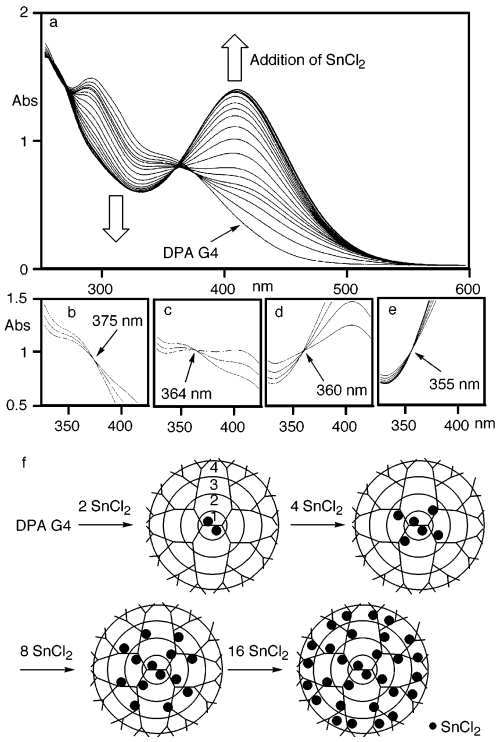

Figure 2. UV−vis spectra of DPA G4 (5×10^{-6} M) complexed with (a) 0−30, (b) 0−2, (c) 3−6, (d) 7−14, and (e) 15−30 equiv of $SnCl_2$ (solvent 1:1 dichloromethane:acetonitrile), and (f) schematic representation of stepwise radial complexation of DPA G4 with $SnCl_2$.

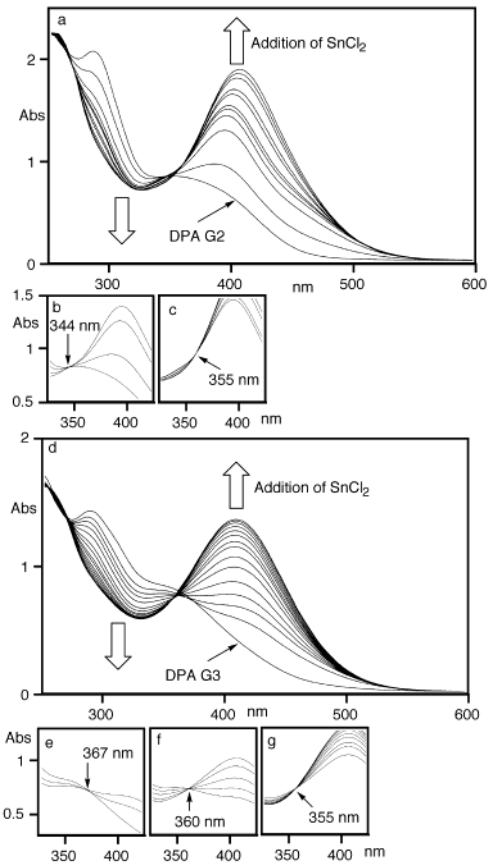

Figure 3. UV−vis spectra of DPA G2 (3×10^{-5} M) complexed with (a) 0−6, (b) 0−2, and (c) 3−6 equiv of $SnCl_2$ and DPA G3 (1×10^{-5} M) complexed with (d) 0−14, (e) 0−2, (f) 3−6, and (g) 7−14 equiv of $SnCl_2$ (solvent 1:1 dichloromethane:acetonitrile).

Results and Discussion

1. Stepwise Radial Complexation in DPAs. Imine groups coordinate strongly to various metal ions. The fourth generation of a dendritic polyphenylazomethine (DPA G4) having 30 imine groups should trap 30 equiv of $SnCl_2$, because an imine group is complexed with $SnCl_2$ at a ratio of 1:1. Addition of $SnCl_2$ to a dichloromethane/acetonitrile solution of DPA G4 resulted in a color change from yellow to orange due to complexation. The UV−vis spectral change shows that the complexation is finished within 10 min after addition of $SnCl_2$. Using UV−vis spectroscopy to monitor the titration until 30 equiv of $SnCl_2$ had been added, we observed four time changes in the position of the isosbestic point (Figure 2a), indicating that the complexation proceeds not randomly but stepwise. An isosbestic point appears when a compound is quantitatively transformed into another by complexation,[5] so the four shifts in the isosbestic point suggest that four different complexes are successively formed on $SnCl_2$ addition. The spectra of DPA G4 gradually changed, with an isosbestic point at 375 nm up to the addition of 2 equiv of $SnCl_2$ (Figure 2b). The isosbestic point then shifted on further addition of $SnCl_2$ and appeared at 364 nm between 3 and 6 equiv (Figure 2c). While adding between 7 and 14 equiv of $SnCl_2$, an isosbestic point appeared at 360 nm, moving to 355 nm on adding between 15 and 30 equiv (Figure 2d and 2e). Overall, the isosbestic point shifted about 20 nm from 375 to 355 nm, and the number of added equivalents of $SnCl_2$ required to induce a shift was in agreement with the number of imine sites present in the different shells of DPA G4. From a kinetic standpoint, complexation of the terminal imines of the dendrimer is expected to occur first. However, the titration results suggest that, on the time scale of our observations, the process is thermodynamically controlled and proceeds in a stepwise fashion from the core imines to the terminal imines of DPA G4 (Figure 2f).

Similar stepwise complexation was also observed with DPA G2 and G3 (Figure 3). For DPA G2, two isosbestic points appeared at 344 and 355 nm on adding 0−2 and 3−6 equiv of $SnCl_2$, respectively. For DPA G3, three isosbestic points appeared at 367, 360, and 355 nm on adding between 0 and 2, 3−6, and 7−14 equiv of $SnCl_2$, respectively. Again, the equivalents of $SnCl_2$ added before a shift in isosbestic point is observed agree with the number of imine sites present in the different shells of the two dendrimers. These results further supported the idea that metal ions are incorporated in a stepwise fashion, filling first the shells close to the dendrimer core and

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then progressively the more peripheral shells. The spectral changes accompanying the addition of $SnCl_2$ to the G4 dendron and the linear phenylazomethine dimer and trimer[6] resulted in each case in the appearance of only one isosbestic point. This behavior shows that the complexation between $SnCl_2$ molecules and the imine sites is random. These observations therefore suggest that the stepwise complexation behavior in DPAs does not reflect changes in the basicity of imine groups induced by complexation at neighboring imine groups. If that were the case, we would also expect to see stepwise complexation when titrating the G4 dendron and linear oligomers.

On the other hand, the stepwise complexation behavior was not observed in the complexation of DPA G4 with $Eu(OTf)_3$ or $La(OTf)_3$. In the complexation of DPA G4 with $Eu(OTf)_3$, the spectrum changed significantly on addition of a small amount of $Eu(OTf)_3$ to the solution of DPA G4. This phenomenon shows that a $Eu(OTf)_3$ molecule, which has multicoordination sites, is complexed with several imine sites of DPA G4. Therefore, stepwise complexation was not observed, but the spectral change continued up to the addition of 30 equiv of $Eu(OTf)_3$. This result shows that the complexation occurs randomly and that the Eu salt is finally complexed with the imine site in a ratio of 1:1. In the complexation of DPA G4 with $La(OTf)_3$, the spectrum changed up to the addition of 8 equiv of $La(OTf)_3$. The large size of $La(OTf)_3$ prevents complexation due to the crowded exterior of the dendrimer.

2. Shell-Selective Reduction (SSR) of Imines in DPAs. As a novel method for confirming the stepwise complexation, except for UV−vis spectral measurements, we exploited a novel shell-selective reduction (SSR) method for imines in DPAs. Because reduction of imines to amines is accelerated by complexation with $SnCl_2$, only the imine groups complexed with $SnCl_2$ in DPAs should be reduced during the reduction of the complexes. Therefore, the positions of $SnCl_2$ molecules in the DPA complexes are exactly determined by identification of the product after reduction of the complex. During the reduction of DPA G1 complexed with 2 equiv of $SnCl_2$ in the presence of $NaBH_4$, the two imine sites were quickly and quantitatively reduced to amines. Interestingly, during the reduction of DPA G2 complexed with 2 equiv of $SnCl_2$, only two imines at the first shell were selectively reduced to amines (DPA-red G2, a 90% NMR yield, Figure 4). This result clearly supports the idea that 2 equiv of $SnCl_2$ is complexed with the two imines of the first shell in DPA G2 (Figure 4a). In the ^1H NMR spectrum of DPA G2, two pairs of doublet peaks (1 trans, 1cis) attributed to the first shell of the *C*-connected phenyl rings appear based on the *cis*- or *trans*-conformation for the core phenyl ring (Figure 4b).[7] On the other hand, in the spectrum of the reduced product, DPA-red G2, only one pair of doublet peaks (1) attributed to the *C*-connected phenyl rings appears due to the disappearance of the regioconformation and one pair of doublet peaks (*x*, *y*) attributed to the reduced imines appears around 5.2 ppm (Figure 4c).

The TOF-MS measurement is also useful in determining the positions of the amine groups in DPA-red G2, because the fragment peak based on easy cleavage of the C−N single bond

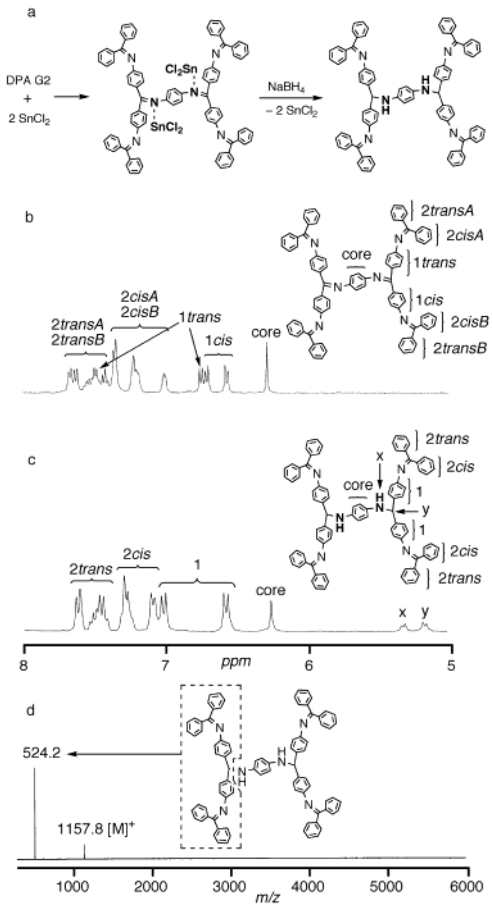

Figure 4. (a) Shell-selective reduction of imines in DPA G2 complexed with 2 equiv of $SnCl_2$. The ^1H NMR spectra (400 MHz, DMSO-d_6) of (b) DPA G2 and (c) the main product obtained by reduction of the complex (DPA-red G2). (d) MALDI-TOF-MS spectrum of DPA-red G2.

appears in the spectrum. In the spectrum of DPA-red G2, the fragment peak at 524.2 shows the cleavage of the C−N single bond at the first shell (Figure 4d).

The SSR of the imines was also performed with DPA G4 (Figure 5). During the reduction of DPA G4 complexed with 2 equiv of $SnCl_2$, the imines at the first shell were selectively reduced to amines. In the ^1H NMR spectrum of DPA G4, a singlet peak attributed to the core protons did not appear due to the fixed conformation of the core by the bulky G4 dendrons (Figure 5a).[4b] On the other hand, a singlet peak attributed to the core protons appeared in the spectrum of the crude product obtained by reduction of DPA G4 complexed with 2 equiv of $SnCl_2$ (DPA-red G4, Figure 5b). This result supports the idea that two molecules of $SnCl_2$ are complexed with the two imines in the first shell of a DPA G4 molecule. The TOF-MS spectrum of DPA-red G4 also clearly supported that the amine groups are at the first shell; a fragment peak at 2674.9 appears based on the cleavage of the C−N single bond at the first shell (Figure 5c).

3. Stepwise Complexation Behavior in NMR Measurement. The stepwise complexation behavior in DPAs with $SnCl_2$ was also supported by ^1H NMR measurement (Figure 6). In the spectrum of DPA G2, a singlet peak attributed to the four protons of the core phenyl ring was shifted to a lower magnetic field on addition of $SnCl_2$ due to the coordination to the imine nitrogen. The shift was large up to a 2 equiv addition of $SnCl_2$,

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(7) The peaks were assigned by the combination of H−H COSY, NOESY, C.-H COSY, and HMQC and comparison of the spectra of DPAs.

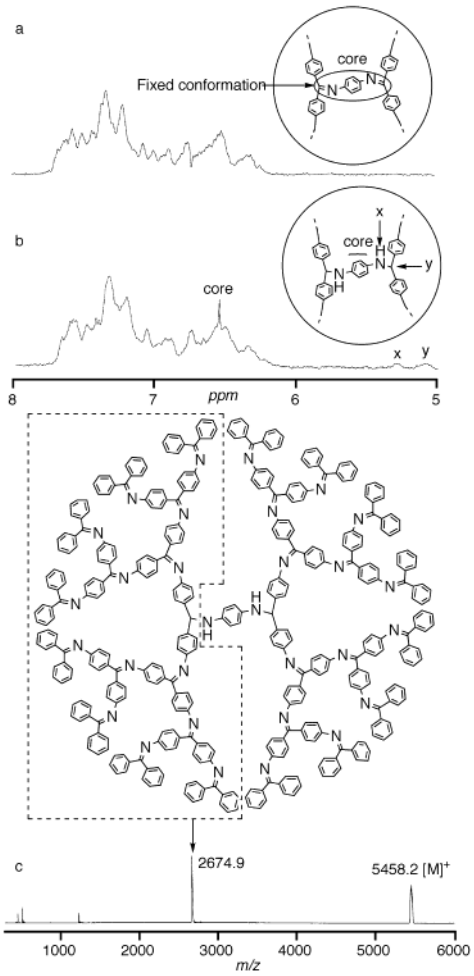

Figure 5. ^{1}H NMR spectra (400 MHz, DMSO-d_6) of (a) DPA G4 and (b) the product obtained by reduction of DPA G4 complexed with 2 equiv of $SnCl_2$ (DPA-red G4). (c) MALDI-TOF-MS spectrum of DPA-red G4.

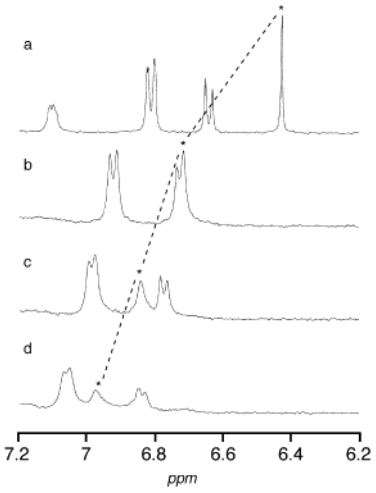

Figure 6. ^{1}H NMR spectra (400 MHz, dichloromethane-d_2/acetonitrile-d_3 = 1:1, 7.2−6.2 ppm only) of (a) DPA G2 and the complex with (b) 2, (c) 4, and (d) 6 equiv of $SnCl_2$. The marked peaks (*) are attributed to the four protons of the core phenyl group in the DPA G2.

and the shift became smaller with the further addition of $SnCl_2$. This spectral change supports the idea that the complexation of $SnCl_2$ first occurs at the core imines in DPA G2.[8]

4. Expanded Molecular Size of DPA G4 by Trapping $SnCl_2$ Molecules. Complexation of DPAs with $SnCl_2$ was also confirmed by atomic absorption spectroscopy (AAS). The atomic absorption spectrum of DPA G4 fully complexed with $SnCl_2$ shows that at least 29 molecules of $SnCl_2$ are trapped in a DPA G4 molecule (Sn content in DPA G4 complexed with 30 equiv of $SnCl_2$; calcd, 31.96%; found, 31.0%). The coordination of imine groups to $SnCl_2$ in the complexes of DPAs was supported by the IR spectral measurement; the absorption attributed to the stretching vibration of the imine bond (1617 cm^{-1}) of DPA G4 was shifted to 1624 cm^{-1} by the complexation; a similar shift was observed in DPAs G1−3.

Molecular modeling of DPA G4 complexed with 30 equiv of $SnCl_2$ was performed based on structural information on bond length, angles, and dihedral angles from the X-ray crystal structures of DPA G2[4b] and the reported imines complexed with $SnCl_2$ (Figure 7a). The result of the modeling shows that (1) a DPA G4 molecule can trap 30 equiv of $SnCl_2$ by conformational changes in the branches and (2) the size of the complex (2.8 × 2.9 × 3.0 nm) is larger than that reported for DPA G4 (2.3 × 2.5 × 2.9 nm).

The expansion of the molecular size by the complexation was confirmed by TEM; the TEM image of DPA G4 fully complexed with $SnCl_2$ shows a round shape with a 2.7-nm diameter (Figure 7b), which is larger than that reported for DPA G4 (2.3 nm).[4b] The stepwise radial complexation was also observed by TEM as a heterogeneous assembly of $SnCl_2$ molecules inside a DPA G4 molecule. In general, organic samples are inverted on RuO_4 vapor before the TEM measurement in order to enhance the contrast of the TEM images, but metal atoms such as tin appear as TEM images without (or after a very short time of) the inversion. Therefore, the assembly of $SnCl_2$ inside DPAs is confirmed by the TEM images of the complex without (or after a very short time of) the inversion. In the TEM image of DPA G4 complexed with 14 equiv of $SnCl_2$ [the sample was inverted on RuO_4 vapor for a very short time (within 1 min)], the assembly of $SnCl_2$ was observed as a round shape with a 2.0-nm diameter (Figure 7c). The 2.0-nm diameter is smaller than that in DPA G4. This result directly supports the idea that 14 equiv of $SnCl_2$ molecules is complexed with the imines not randomly but stepwise up to the third shell of DPA G4. After the full inversion (more than 15 min), a DPA G4 molecule complexed with 14 equiv of $SnCl_2$ was confirmed to be a round shape with a 2.5-nm diameter, which shows the whole size of the complex.

5. Gradients in a Basicity of Imine Groups in DPAs. The stepwise complexation behavior in DPAs suggests that the basicity of the core imines is higher than that of the more peripheral imines,[9] which was confirmed in the ^{13}C NMR spectra as a high magnetic field shift of the peak attributed to the core imine carbon. The marked (*) peaks in the spectra of DPAs were attributed to the core imine carbon (Figure 8), which were determined by the SSR method and the comparison of their spectra. In the spectra of DPA G2 and G3, the marked peaks are shifted by more than 1 ppm toward a high magnetic field, relative to the peaks attributed to an imine carbon at the periphery (Figure 8a−c). These spectra show that the basicity

(8) In the ^{1}H NMR spectra of DPA G2, the peaks attributed to the outer shell's protons become much broader on addition of $SnCl_2$ due to the increase of steric hindrance. Therefore, the magnitude of the shift in the outer shell's protons was not able to be measured on addition of the higher amounts of $SnCl_2$.

(9) Hecht, S.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1999**, *121*, 4084.

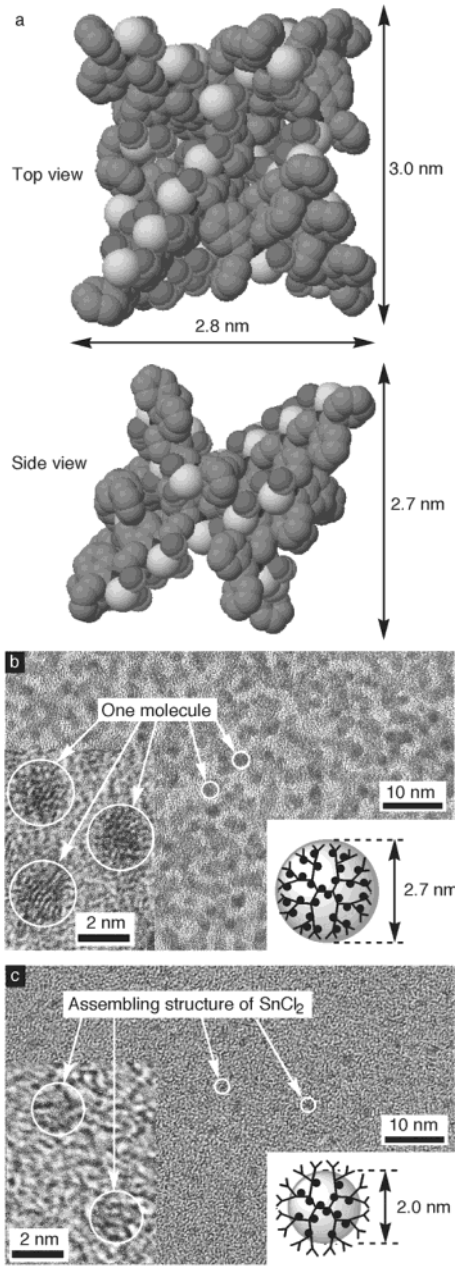

Figure 7. (a) Molecular modeling of DPA G4 complexed with 30 equiv of $SnCl_2$. TEM images of (b) DPA G4 complexed with 30 equiv of $SnCl_2$, and (c) DPA G4 complexed with 14 equiv of $SnCl_2$, which was inverted on RuO_4 vapor for 1 min.

of the core imines is enhanced by the electron-releasing effect of the more peripheral imines. Therefore, introduction of electron-withdrawing or -releasing groups to the core of DPAs is expected to change the gradient of basicity among the shells of DPAs. We synthesized novel DPAs having a 2,3,5,6-tetrafluoro-, 2,5-dichloro-, 2,5-dimethyl-substituted phenyl ring at the core (DPA-F G1−3, DPA-Cl G1−3, and DPA-Me G1−2) via dehydration of the DPA dendrons with tetrafluoro-, 2,5-dichloro-, and 2,5-dimethyl-*p*-phenylenediamine, respectively (Figure 1).[10]

(10) DPA-Me G3 was not obtained at all under the synthetic conditions. The preferential formation of the core compound combined with only one DPA G3 dendron indicates steric hindrance between bulky dendrons and methyl groups at the core.

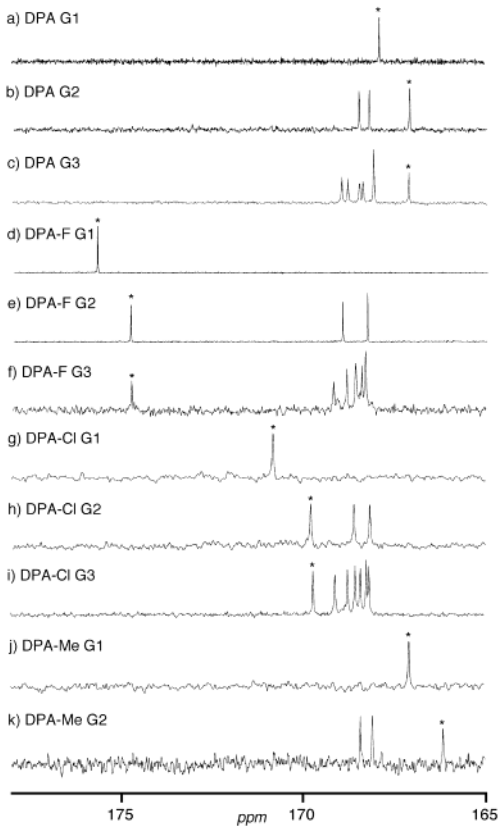

Figure 8. ^{13}C NMR spectra (100 MHz, $CDCl_3$ TMS, ppm, only 165−180 ppm) of (a) DPA G1, (b) DPA G2, (c) DPA G3, (d) DPA-F G1, (e) DPA-F G2, (f) DPA-F G3, (g) DPA-Cl G1, (h) DPA-Cl G2, (i) DPA-Cl G3, (j) DPA-Me G1, and (k) DPA-Me G2. The marked peaks (*) are attributed to core imine carbons.

6. Stepwise Complexation in DPAs Having a Tetrafluorophenyl Core (DPA-F G1−3). Introduction of fluorine to the core in DPAs strongly reduced the basicity of the core imines. The complexation constant of an imine in DPA-F G1 ($\log K = 2.9$, which was determined using UV−vis spectral measurement) was much smaller than that of DPA G1 ($\log K = 5.0$) (Figure 9a). Low basicity of imines in DPA-F G1 is also confirmed by the ^{13}C NMR spectrum; a peak attributed to the core imine in DPA-F G1 appears at 175.75 ppm, which is at a lower magnetic field than that in DPA G1 (167.97 ppm) (Figure 8a and 8d). On adding $SnCl_2$ to DPA-F G2, two isosbestic points appeared at 283 and 286 nm upon adding 0−4 and 5−6 equiv of $SnCl_2$, respectively (Figure 9b−d). This result shows that the imines present in the second shell were completed first and then those present in the first shell, whose basicity was lowered by the electron-withdrawing tetrafluorophenyl group (Figure 10a). On adding $SnCl_2$ to DPA-F G3, three isosbestic points appeared at 356. 366, and 368 nm upon adding 0−4, 5−12, and 13−14 equiv of $SnCl_2$, respectively (Figure 9e−h). That is, the imines present in the second shell were completed first, then those present in the third shell, and finally those present in the first shell (Figure 10b).

This "reversed" pattern of complexation in DPA-F G2 was also confirmed by the SSR method (Figure 11). The reduction of DPA-F G2 complexed with 4 equiv of $SnCl_2$ gave DPA-F G2 having four amines at the second shell (DPA-F-red G2, an 80% NMR yield). This result shows that 4 equiv of $SnCl_2$ is complexed with the four imines of the second shell in DPA-F

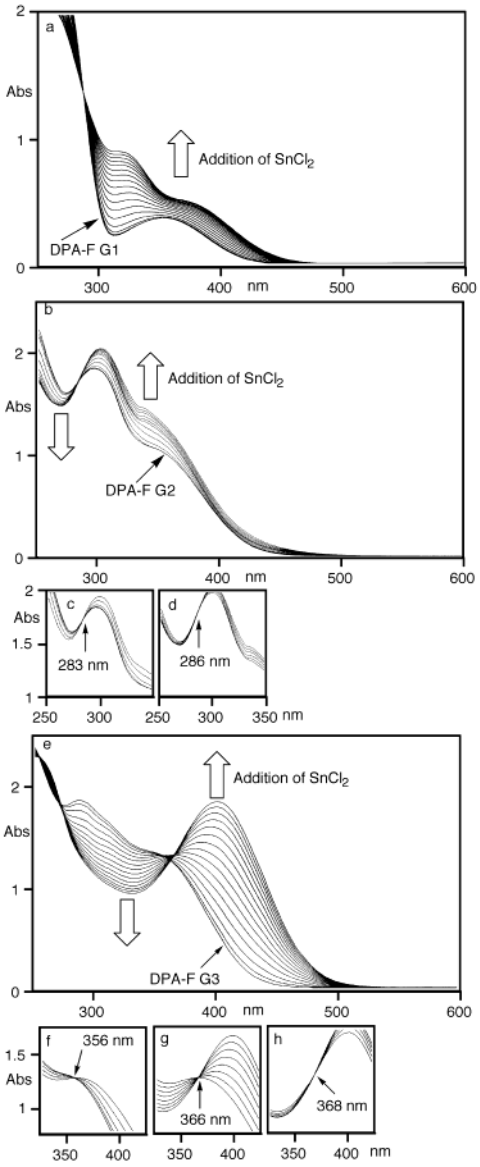

Figure 9. UV−vis spectra of (a) DPA-F G1 (6×10^{-5} M) complexed with $SnCl_2$, DPA-F G2 (3×10^{-5} M) complexed with (b) 0−8, (c) 0−4, and (d) 5−8 equiv of $SnCl_2$, and DPA-F G3 (1×10^{-5} M) complexed with (e) 0−18, (f) 0−4, (g) 5−12, and (h) 13−18 equiv of $SnCl_2$ (solvent 1:1 dichloromethane:acetonitrile).

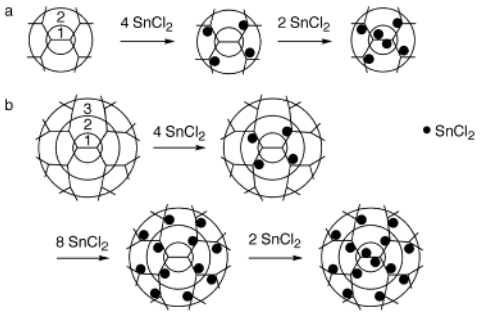

Figure 10. Schematic representation of stepwise complexation of (a) DPA-F G2 and (b) G3 with $SnCl_2$.

G2 (Figure 11a). In the ^{1}H NMR spectrum of DPA-F G2, four sets of peaks (2 transA, 2 cisA, 2 transB, 2 cisB) attributed to the second shell of the *C*-connected phenyl rings appear based on the *trans,trans*-, *trans,cis*-, *cis,trans*-, and *cis,cis*-conformation

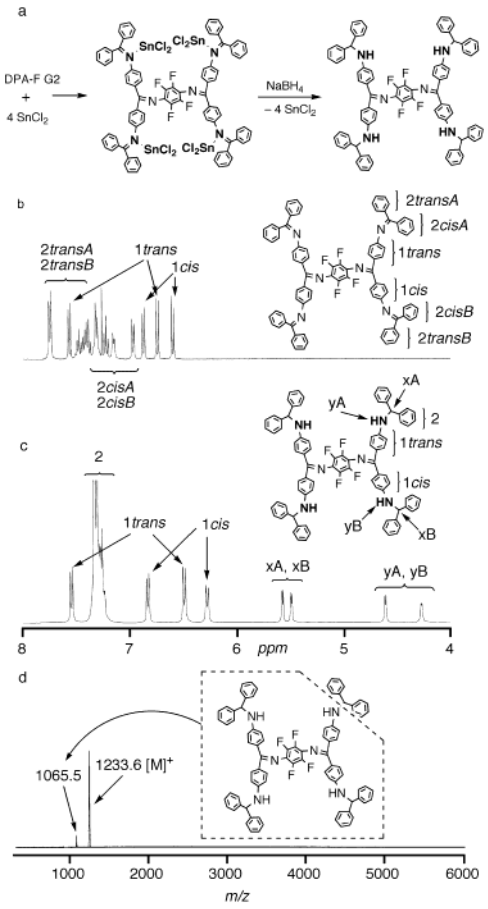

Figure 11. (a) Reduction of imines in DPA-F G2 complexed with 4 equiv of $SnCl_2$. ^{1}H NMR spectra (400 MHz, DMSO-d_6) of (b) DPA-F G2, and (c) the main product obtained by reduction of the complex. (d) MALDI-TOF-MS spectrum of DPA-F-red G2.

for the core phenyl ring and the first shell of the *C*-connected phenyl ring, respectively (Figure 11b). On the other hand, in the spectrum of the product, DPA-F-red G2, peaks (2) attributed to the second shell of *C*-connected phenyl rings became simple due to the disappearance of the regioconformation for the first shell of the *C*-connected phenyl ring and two pairs of doublet peaks (*x*A, *y*A, *x*B, *y*B) attributed to the reduced imines appears between 4.2 and 5.6 ppm due to the *cis*- or *trans*-conformation for the core phenyl ring (Figure 11c). Two peaks at 169.03 and 168.36 ppm in the ^{13}C NMR spectrum of DPA-F G2 (Figure 8e) disappeared in the spectrum of DPA-F-red G2, which shows that their peaks are attributed to the terminal imines in DPA-F G2. The positions of amines in DPA-F-red G2 are also confirmed by the TOF-MS spectra. In the TOF-MS spectrum, the fragment peak at 1065.5 shows the cleavage of the C−N single bond at the second shell (Figure 11d).

7. DPAs Having a 2,5-Dichlorophenyl Core (DPA-Cl G1−3). Introduction of chlorine to the core of DPAs also reduced the basicity of the core imines. The complexation constant of an imine in DPA-Cl G1 ($\log K = 4.3$) was between those of DPA-F G1 and DPA G1 (Figure 12a). In the ^{13}C NMR spectrum, a peak attributed to the core imine in DPA-Cl G1 appears at 170.85 ppm, which also exists between those of DPA G1 and DPA-F G1 (Figure 8g). On adding $SnCl_2$ to DPA-Cl G2, two isosbestic points appeared at 315 and 294 nm upon adding 0−4 and 5−6 equiv of $SnCl_2$, respectively (Figure 12b−

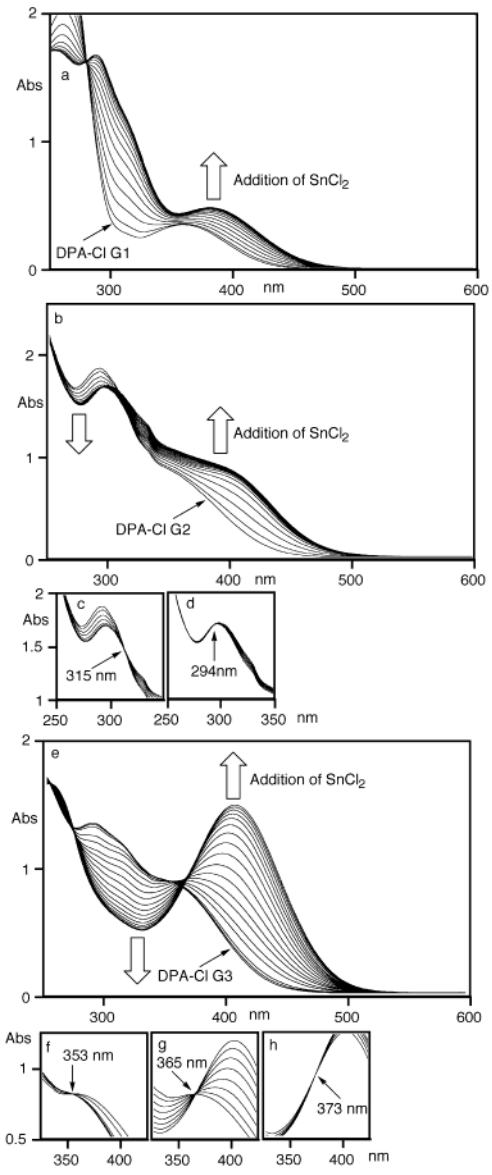

Figure 12. UV−vis spectra of (a) DPA-Cl G1 (6×10^{-5} M) complexed with $SnCl_2$, DPA-Cl G2 (3×10^{-5} M) complexed with (b) 0−6, (c) 0−4, and (d) 5−6 equiv of $SnCl_2$, and DPA-Cl G3 (1×10^{-5} M) complexed with (e) 0−18, (f) 0−4, (g) 5−12, and (h) 13−18 equiv of $SnCl_2$ (solvent 1:1 dichloromethane:acetonitrile).

d). This result shows the "reverse" complexation pattern, which is the same as that in DPA-F G2. When adding $SnCl_2$ to DPA-Cl G3, three isosbestic points appeared at 353, 365, and 373 nm upon adding 0−4, 5−12, and 13−14 equiv of $SnCl_2$, respectively (Figure 12e−h). This result shows that the complexation pattern is in the order of the second, third, and first shells.

8. DPAs Carrying a Dimethylphenyl Core (DPA-Me). Unlike DPA-F and DPA-Cl, introduction of methyl groups to the core enhanced the basicity of the core imines. The complexation constant of an imine in DPA-Me G1 (log K = 5.4) was higher than that in DPA G1 (Figure 13a). The higher basicity of imines in DPA-Me G1 than that in DPA G1 is also confirmed by ^{13}C NMR measurement; a peak attributed to the core imine in DPA-Me G1 appears at 167.10 ppm, which is at a higher magnetic field than that of DPA G1 (Figure 8j). On adding $SnCl_2$ to DPA-Me G2, two isosbestic points appeared

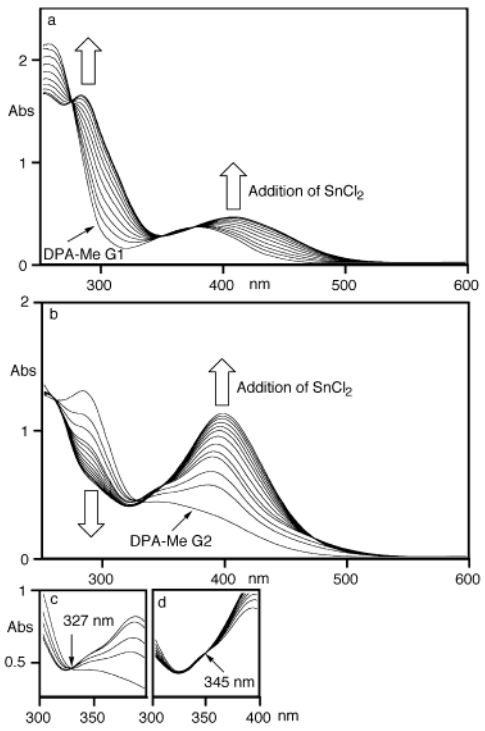

Figure 13. UV−vis spectra of (a) DPA-Me G1 (6×10^{-5} M) complexed with $SnCl_2$, and UV−vis spectra of DPA-Me G2 (3×10^{-5} M) complexed with (b) 0−6, (c) 0−2, and (d) 3−6 equiv of $SnCl_2$ (solvent 1:1 dichloromethane:acetonitrile).

at 327 and 345 nm upon adding 0−2 and 3−6 equiv of $SnCl_2$, respectively (Figure 13b−d). This behavior is similar to that of DPA G2 and shows the "normal" stepwise complexation pattern.

As a result, the complexation pattern in DPA derivatives is supported by the ^{13}C NMR spectra. In the spectra of DPA-F and DPA-Cl, whose complexation pattern is in the order of the second, third, and first shells, the chemical shifts attributed to a core imine carbon is at a lower magnetic field than that of a branch imine carbon (around 168 ppm) (Figure 8e−i). On the other hand, in the spectra of DPA and DPA-Me, whose complexation pattern is in the order of the first, second, and third shells, the chemical shifts attributed to the core imine carbons are at a higher magnetic field (Figure 8b, c, and k).

Conclusions

The stepwise radial complexation in dendritic polyphenylazomethines (DPAs) with $SnCl_2$ was observed as a stepwise shift in the isosbestic point in the UV−vis spectra. The number of added equivalents of $SnCl_2$ required to induce a shift was in agreement with the number of imine groups present in the different shells of the DPAs. These spectral changes suggest that the complexation is proceeding in a stepwise fashion from the core imines to the terminal imines of the DPAs. The stepwise complexation was also supported using TEM, NMR, and shell-selective reduction (SSR) of the imines. An expansion of the molecular size of DPA G4 by complexation was confirmed by molecular modeling and TEM measurements. The stepwise complexation is caused by a gradient in the basicity of the imine groups among the shells, which was revealed by the different chemical shift of the imine carbon in the ^{13}C NMR spectra. Therefore, the order of complexation among the shells permits control by the introduction of electron-withdrawing or -releasing

groups; the complexation in DPA derivatives having electron-withdrawing groups at the core proceeded in the order of the second, third, and first.

Experimental Section

General Methods. All reagents and solvents were purchased from commercial sources and were further purified by the standard methods, if necessary. In particular, acetonitrile, dehydrated (cat. no. 01837-25, Kanto Chemical Co., Inc.), and dichloromethane, dehydrated (cat. no. 11338-25, Kanto Chemical Co., Inc.), were used as solvents in UV−vis spectral measurement. UV−vis spectra were obtained using Shimadzu UV-3150, UV-3100PC, and UV-2400PC spectrophotometers. NMR spectra were recorded on JEOL JNM-GX400α (400 MHz) and JNM-GX400 (400 MHz) spectrometers with tetramethylsilane as an internal standard. Infrared spectra were obtained with JASCO FT/IR-460plus. TOF-MS spectra were run on a Shimadzu KOMPACT SEQ mass spectrometer.

TEM Measurements. The chloroform solution (0.2 mg/mL) of DPA G4 complexed with 14 or 30 equiv of $SnCl_2$ was deposited on carbon-coated copper grids, and the grids were inverted on RuO_4 vapor. The TEM images were obtained at 120 kV with a JEOL JEM-2010 at a magnification of 300000× and 1200000×. The image was enlarged 4 times and printed, then scanned into the computer, and analyzed with TIFF image.

Synthesis of DPA-F G1. Benzophenone (1.21 g, 6.66 mmol), tetrafluoro-*p*-phenylenediamine (200 mg, 1.11 mmol), and 1,4-diazabicyclo[2.2.2]octane (DABCO) (747 mg, 6.66 mmol) were dissolved in chlorobenzene (50 mL). Titanium(IV) tetrachloride (316 mg, 1.67 mmol) was added to the solution using a dropping funnel. The dropping funnel was rinsed with chlorobenzene (5 mL). The reaction mixture was heated in an oil bath at 125 °C for 24 h. A precipitate was removed by filtration. The filtrate was concentrated, and DPA-F G1 (144 mg, 0.28 mmol, 25%) was isolated by silica gel column chromatography (1:20−1:15 ethyl acetate:hexane, R_f = 0.75 in the solution of 1:3:5 ethyl acetate:dichloromethane:hexane). DPA-F G1: ^{1}H NMR (400 MHz, $CDCl_3$, TMS standard, ppm): δ 7.75 (d, J = 7.6 Hz, 4H), 7.51 (t, J = 7.6 Hz, 2H), 7.41 (dd, J = 7.6, 7.6 Hz, 4H), 7.38 (t, J = 7.6 Hz, 2H), 7.29 (dd, J = 7.6, 7.6 Hz, 4H), 7.11 (d, J = 7.6 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS standard, ppm): δ 175.75, 138.74−138.49 (m), 137.72, 136.30−136.05 (m), 135.98, 131.72, 129.70, 129.31, 128.19, 128.08, 127.43, 125.81−125.47 (m). IR (KBr, cm^{-1}): 1610 (C═N), 1594 (phenyl), 993, 969, 698. MALDI-TOF-MS: calcd 509.5 $[M+H]^+$, found 509.4. Anal. Calcd for $C_{32}H_{20}F_4N_2$: C, 75.6; H, 3.96; N, 5.51. Found: C, 75.6; H, 3.94; N, 5.62.

Synthesis of DPA-F G2. DPA G2 dendron (1.50 g, 2.77 mmol), tetrafluoro-*p*-phenylenediamine (166 mg, 0.92 mmol), and DABCO (663 mg, 5.54 mmol) were dissolved in chlorobenzene (50 mL). Titanium(IV) tetrachloride (263 mg, 1.39 mmol) was added to the solution using a dropping funnel. The dropping funnel was rinsed with chlorobenzene (5 mL). The reaction mixture was heated in an oil bath at 125 °C for 24 h. A precipitate was removed by filtration. The filtrate was concentrated, and DPA-F-G2 (123 mg, 0.10 mmol, 11%) was isolated by GPC (chloroform, R_f = 0.78 in the solution of 1:3:3 ethyl acetate:dichloromethane:hexane). DPA-F G2: ^{1}H NMR (400 MHz, $CDCl_3$, TMS standard, ppm): δ 7.75 (d, J = 7.2 Hz, 8H), 7.57 (d, J = 8.4 Hz, 4H), 7.50−7.30 (m, 20H), 7.22 (dd, J = 7.2, 7.2 Hz, 4H), 7.15 (br, 4H), 6.97 (d, J = 7.2 Hz, 4H), 6.87 (d, J = 8.4 Hz, 4H), 6.74 (d, J = 8.4 Hz, 4H), 6.60 (d, J = 8.4 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS standard, ppm): δ 174.79, 169.03, 168.36, 154.36, 152.47, 139.06, 138.87, 138.75−138.55 (m), 136.36−136.24 (m), 135.58, 135.33, 132.87, 130.88, 130.76, 130.44, 129.29, 129.24, 129.20, 128.82, 128.76, 128.54, 128.23, 128.08, 128.03, 127.97, 127.69, 125.77−125.54 (m), 120.40, 120.34, 120.27. IR (KBr, cm^{-1}): 1618 (C═N), 1587 (phenyl), 978, 697. MALDI-TOF-MS: calcd 1225.4 $[M]^+$, found 1225.5.

Synthesis of DPA-F G3. DPA G3 dendron (4.01 g, 3.19 mmol), tetrafluoro-*p*-phenylenediamine (287 mg, 1.59 mmol), and DABCO (1.07 g, 9.57 mmol) were dissolved in chlorobenzene (200 mL). Titanium(IV) tetrachloride (98.3 mg, 2.39 mmol) was added to the solution using a dropping funnel. The dropping funnel was rinsed with chlorobenzene (5 mL). The reaction mixture was heated in an oil bath at 125 °C for 24 h. A precipitate was removed by filtration. The filtrate was concentrated, and DPA-F G3 (112 mg, 42.1 μmol, 3%) was isolated by silica gel column chromatography (1:2:5−1:1:3 ethyl acetate: dichloromethane:hexane, R_f = 0.27 in the solution of 1:1:3 ethyl acetate: dichloromethane:hexane). DPA-F G3 (refine data): ^{1}H NMR (400 MHz, $CDCl_3$, TMS standard, 30 °C, ppm): δ 7.74−6.50 (m, 128H). ^{13}C NMR (100 MHz, $CDCL_3$, TMS standard, 30 °C, ppm): δ 174.74, 169.17, 169.07, 168.81, 168.56, 168.40, 168.28, 154.93, 153.85, 153.68, 152.65, 152.19, 152.07, 139.35, 139.30, 139.12, 139.05, 136.79, 135.83, 135.68, 135.45, 134.29, 134.19, 132.64, 132.40, 130.95, 130.75, 130.64, 130.42, 130.18, 130.14, 130.06, 129.42, 129.24, 128.86, 128.65, 128.22, 128.12, 128.06, 127.89, 127.78, 121.05, 120.77, 120.54, 120.50, 120.38, 120.07. IR (KBr, cm^{-1}): 1618 (C═N), 1578 (phenyl), 959, 849, 695. MALDI-TOF-MS: calcd 2659.1 $[M]^+$, found 2659.3.

Synthesis of DPA-Cl G1. Benzophenone (308 mg, 1.68 mmol), 2,5-dichloro-1,4-phenylenediamine (100 mg, 0.56 mmol), and DABCO (380 mg, 3.38 mmol) were dissolved in chlorobenzene (30 mL). Titanium-(IV) tetrachloride (160 mg, 0.85 mmol) was added to the solution using a dropping funnel. The dropping funnel was rinsed with chlorobenzene (5 mL). The reaction mixture was heated in an oil bath at 125 °C for 24 h. A precipitate was removed by filtration. The filtrate was concentrated, and DPA-Cl G1 (43 mg, 0.08 mmol, 15%) was isolated by GPC (chloroform, R_f = 0.74 in the solution of 1:3:5 ethyl acetate: dichloromethane:hexane). DPA-Cl G1: ^{1}H NMR (400 MHz, $CDCl_3$, TMS standard, ppm): δ 7.74 (d, J = 7.6 Hz, 4H), 7.49 (t, J = 7.6 Hz, 2H), 7.40 (dd, J = 7.6, 7.6 Hz, 4H), 7.33 (t, J = 7.6 Hz, 2H), 7.27 (dd, J = 7.6, 7.6 Hz, 4H), 7.09 (d, J = 7.6 Hz, 4H), 6.51 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS standard, ppm): δ 170.85, 144.66, 138.49, 135.70, 131.12, 129.44, 128.89, 128.40, 128.13, 127.96, 123.32, 121.45. IR (KBr, cm^{-1}): 1608 (C═N), 1593 (phenyl), 957, 874, 698. MALDI-TOF-MS: calcd 505.4 $[M]^+$, found 505.4.

Synthesis of DPA-Cl G2. DPA G2 dendron (1.50 g, 2.77 mmol), 2,5-dichloro-1,4-phenylenediamine (122 mg, 0.69 mmol), and DABCO (934 mg, 9.32 mmol) were dissolved in chlorobenzene (50 mL). Titanium(IV) tetrachloride (391 mg, 2.08 mmol) was added to the solution using a dropping funnel. The dropping funnel was rinsed with chlorobenzene (5 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, and DPA-Cl G2 (152 mg, 0.15 mmol, 18%) was isolated by silica gel column chromatography (1:1:15−1:1:12 ethyl acetate:dichloromethane:hexane, R_f = 0.72 in the solution of 1:3:3 ethyl acetate:dichloromethane:hexane). DPA-Cl G2: ^{1}H NMR (400 MHz, $CDCl_3$, TMS standard, ppm): δ 7.75 (d, J = 8.4 Hz, 4H), 7.72 (d, J = 8.4 Hz, 4H), 7.52 (d, J = 8.4 Hz, 4H), 7.49−7.21 (m, 24H), 7.15 (d, J = 8.4 Hz, 4H), 6.99 (d, J = 8.4 Hz, 4H), 6.84 (d, J = 8.4 Hz, 4H), 6.73 (d, J = 8.4 Hz, 4H), 6.58 (d, J = 8.4 Hz, 4H), 6.42 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS standard, ppm): δ 169.88, 168.70, 168.27, 153.73, 151.85, 144.66, 139.17, 139.07, 135.66, 135.37, 133.67, 130.79, 130.68, 130.50, 130.11, 129.28, 128.73, 128.07, 128.01, 127.93, 127.80, 123.34, 121.56, 120.39, 120.31, 116.60. IR (KBr, cm^{-1}): 1609 (C═N), 1587 (phenyl), 958, 849, 697. MALDI-TOF-MS: calcd 1222.3 $[M]^+$, found 1222.6. Anal. Calcd for $C_{84}H_{58}N_6Cl_2$: C, 82.5; H, 4.78; N, 6.88. Found: C, 82.3; H, 4.81; N, 6.76.

Synthesis of DPA-Cl G3. DPA G3 dendron (3.06 g, 2.44 mmol), 2,5-dichloro1,4-phenylenediamine (323 mg, 1.83 mmol), and DABCO (1.23 g, 11.0 mmol) were dissolved in chlorobenzene (200 mL). Titanium(IV) tetrachloride (346 mg, 1.83 mmol) was added to the solution using a dropping funnel. The dropping funnel was rinsed with chlorobenzene (5 mL). The reaction mixture was heated in an oil bath at 125 °C for 24 h. A precipitate was removed by filtration. The filtrate

was concentrated, and DPA-Cl G3 (159 mg, 60.0 μmol, 3%) was isolated by GPC (chloroform, $R_f = 0.34$ in the solution of 1:2 ethyl acetate:hexane). DPA-Cl G3: ^{1}H NMR (400 MHz, $CDCl_3$, TMS standard, ppm): δ 7.76−7.66 (m, 16H), 7.51−6.98 (m, 76H), 6.87 (d, $J = 8.0$ Hz, 4H), 6.79 (d, $J = 8.0$ Hz, 4H), 6.74 (d, $J = 8.0$ Hz, 8H), 6.69 (d, $J = 8.0$ Hz, 4H), 6.62 (d, $J = 8.0$ Hz, 4H), 6.56 (d, $J = 8.0$ Hz, 8H), 6.49 (d, $J = 8.0$ Hz, 4H), 6.38 (d, $J = 1.2$ Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS standard, ppm): δ 169.69, 169.09, 168.74, 168.53, 168.38, 168.21, 168.15, 154.29, 153.78, 153.65, 152.07, 152.01, 145.05, 139.35, 139.30, 139.10, 135.83, 135.70, 135.54, 134.37, 134.27, 133.37, 130.90, 130.57, 130.39, 130.13, 129.59, 129.40, 129.36, 128.85, 128.71, 128.20, 128.06, 127.91, 127.81, 124.46, 121.47, 121.12, 120.76, 120.53, 120.31, 120.20. IR (KBr, cm^{-1}): 1619 (C═N), 1578 (phenyl), 958, 848, 695. MALDI-TOF-MS: calcd 2656.0 $[M]^+$, found 2656.0.

Synthesis of DPA-Me G1. Benzophenone (2.67 g, 14.7 mmol), 2,5-dimethyl-1,4-phenylenediamine (500 mg, 3.67 mmol), and DABCO (2.47 g, 22.0 mmol) were dissolved in chlorobenzene (50 mL). Titanium(IV) tetrachloride (1.04 g, 5.50 mmol) was added to the solution using a dropping funnel. The dropping funnel was rinsed with chlorobenzene (5 mL). The reaction mixture was heated in an oil bath at 125 °C for 24 h. A precipitate was removed by filtration. The filtrate was concentrated, and DPA-Me G1 (596 mg, 1.28 mmol, 35%) was isolated by silica gel column chromatography (1:1:5 ethyl acetate: dichloromethane:hexane, $R_f = 0.62$ in the solution of 1:3:5 ethyl acetate: dichloromethane:hexane). DPA-Me G1: ^{1}H NMR (400 MHz, $CDCl_3$, TMS standard, ppm): δ 7.73 (d, $J = 7.6$ Hz, 4H), 7.45 (t, $J = 7.6$ Hz, 2H), 7.38 (dd, $J = 7.6$, 7.6 Hz, 4H), 7.28 (t, $J = 7.2$ Hz, 2H), 7.22 (dd, $J = 7.2$, 7.2 Hz, 4H), 7.03 (d, $J = 7.2$ Hz, 4H), 6.17 (s, 2H), 1.92 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS standard, ppm): δ 167.10, 145.54, 139.65, 136.44, 130.24, 129.06, 128.88, 128.24, 127.96, 127.66, 125.48, 121.08, 17.78. IR (KBr, cm^{-1}): 1608 (C═N), 1594 (phenyl), 958, 873, 695. MALDI-TOF-MS: calcd 464.6 $[M]^+$, found 464.5. Anal. Calcd for $C_{34}H_{28}N_2$: C, 87.9; H, 6.07; N, 6.03. Found: C, 87.6; H, 5.99; N, 5.98.

Synthesis of DPA-Me G2. DPA G2 dendron (1.25 g, 2.44 mmol), 2,5-dimethyl-1,4-phenylenediamine (83 mg, 0.61 mmol), and DABCO (410 mg, 3.66 mmol) were dissolved in chlorobenzene (50 mL). Titanium(IV) tetrachloride (173 mg, 0.92 mmol) was added to the solution using a dropping funnel. The dropping funnel was rinsed with chlorobenzene (5 mL). The reaction mixture was heated in an oil bath at 125 °C for 24 h. A precipitate was removed by filtration. The filtrate was concentrated, and DPA-Me G2 (180 mg, 0.15 mmol, 25%) was isolated by silica gel column chromatography (1:3:5 ethyl acetate: dichloromethane:hexane, $R_f = 0.61$ in the solution of 1:3:3 ethyl acetate: dichloromethane:hexane). DPA-Me G2: ^{1}H NMR (400 MHz, $CDCl_3$, TMS standard, ppm): δ 7.75 (d, $J = 7.6$ Hz, 4H), 7.70 (d, $J = 7.6$ Hz, 4H), 7.47 (d, $J = 8.4$ Hz, 4H), 7.45−7.15 (m, 24H), 6.99 (d, $J = 7.6$ Hz, 8H), 6.77 (d, $J = 8.4$ Hz, 4H), 6.72 (d, $J = 8.4$ Hz, 4H), 6.52 (d, $J = 8.4$ Hz, 4H), 6.17 (s, 2H), 1.57 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS standard, ppm): δ 168.49, 168.16, 166.24, 152.90, 151.39, 145.48, 139.32, 139.09, 135.81, 135.65, 135.59, 135.05, 131.22, 130.71, 130.65, 129.85, 129.66, 129.35, 129.26, 128.65, 128.53, 128.09, 128.01, 127.88, 127.72, 125.36, 124.86, 121.73, 120.29, 119.87, 17.77. IR (KBr, cm^{-1}): 1610 (C═N), 1589 (phenyl), 958, 849, 696. MALDI-TOF-MS: calcd 1181.5 $[M]^+$, found 1181.3.

Reduction of Imines in DPA G1. To the chloroform/acetonitrile (1:1) solution (200 mL) of DPA G1 (1.10 g, 2.53 mmol) and $SnCl_2$ (1.44 g, 7.59 mol), $NaBH_4$ (1.91 g, 50.6 mmol) was added quietly. The reaction mixture was stirred at room temperature for 10 min under nitrogen atmosphere. After the reaction, the crude mixture was washed with water including 1% triethylamine (four times), and the organic layer was dried using Na_2SO_4. The reduced product of DPA G1 (DPA-red G1, 987 mg, 89% yield) was isolated by silica gel column chromatography (4:1:1 hexane:chloroform:ethyl acetate). DPA-red G1: ^{1}H NMR (400 MHz, $CDCl_3$, TMS standard, ppm): δ 7.33 (d, $J = 7.3$ Hz, 8H), 7.28 (dd, $J = 7.3$, 7.3 Hz, 8H), 7.20 (t, $J = 7.3$ Hz, 4H), 6.38 (s, 4H), 5.33 (s, 2H), 3.83 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS standard, ppm): δ 129.25, 129.10, 128.18, 127.99, 127.78, 127.13, 30.54. IR (KBr, cm^{-1}): 3415 (NH), 1510 (phenyl), 741, 695. MALDI-TOF-MS: calcd 440.5 $[M]^+$, found 440.0.

Shell-Selective Reduction of Imines in DPA G2. To the dichloromethane/acetonitrile (1:1) solution (200 mL) of DPA G2 (500 mg, 0.437 mmol) and $SnCl_2$ (165 mg, 0.874 mmol), $NaBH_4$ (64 mg, 1.74 mmol) was added. The reaction mixture was stirred at room temperature for 10 min under nitrogen atmosphere. After the reaction, the crude mixture was washed with water including 1% triethylamine (four times), and the organic layer was dried using Na_2SO_4. DPA G2 having two amines at the first shell (DPA-red G2, 90% NMR yield) was formed as a main product. The separation of DPA-red G2 from the crude products was quite difficult due to very small difference of the R_f values, but DPA-red G2 (40 mg) was isolated by silica gel column chromatography (4:1:1 hexane:chloroform:ethyl acetate). DPA-red G2:^{1}H NMR (400 MHz, DMSO-d_6, TMS standard, ppm): δ 7.62 (d, $J = 7.3$ Hz, 8H), 7.52 (t, $J = 7.3$ Hz, 4H), 7.45 (dd, $J = 7.3$, 7.3 Hz, 8H), 7.32 (t, $J = 7.3$ Hz, 4H), 7.28 (dd, $J = 7.3$, 7.3 Hz, 8H), 7.10 (d, $J = 7.3$ Hz, 8H), 7.02 (d, $J = 8.3$ Hz, 8H), 6.58 (d, $J = 8.3$ Hz, 8H), 6.25 (s, 4H), 5.33 (d, $J = 7.1$ Hz, 2H), 5.16 (d, $J = 7.1$ Hz, 2H). ^{1}H NMR (400 MHz, $CDCl_3$, TMS standard, ppm): δ 7.72 (d, $J = 7.3$ Hz, 8H), 7.45 (t, $J = 7.3$ Hz, 4H), 7.37 (dd, $J = 7.3$, 7.3 Hz, 8H), 7.26 (t, $J = 7.3$ Hz, 4H), 7.20 (dd, $J = 7.3$, 7.3 Hz, 8H), 7.08 (d, $J = 7.3$ Hz, 8H), 7.02 (d, $J = 8.3$ Hz, 8H), 6.64 (d, $J = 8.3$ Hz, 8H), 6.25 (s, 4H), 5.11 (s, 2H), 3.64 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS standard, ppm): δ 169.07, 150.87, 140.58, 140.29, 138.98, 136.75, 131.28, 130.19, 129.89, 129.19, 128.76, 128.40, 128.22, 121.66, 115.32, 63.38. IR (KBr, cm^{-1}): 3410 (NH), 1617 (C═N), 1594 (phenyl), 1510, 959, 697. MALDI-TOF-MS: calcd 1157.5 $[M]^+$, found 1157.0, 524.2, which is a fragment peak based on the cleavage of the C−N single bond in the first shell (calcd 524.7).

Shell-Selective Reduction of Imines in DPA G4. To the dichloromethane/acetonitrile (1:1) solution (70 mL) of DPA G4 (100 mg, 1.83×10^{-5} mol) and $SnCl_2$ (7.0 mg, 3.67×10^{-5} mol), $NaBH_4$ (3.0 mg, 8.4×10^{-5} mol) was added. The reaction mixture was stirred at room temperature for 5 min under nitrogen atmosphere. After the reaction, the crude mixture was washed with water including 5% triethylamine (four times), and the organic layer was dried using Na_2SO_4. Preferential reduction of the first shell of imines in DPA G4 (DPA-red G4) was confirmed by NMR and TOF-MS measurements. DPA-red G4 (crude): ^{1}H NMR (400 MHz, $CDCl_3$, TMS standard, ppm): δ 7.77−6.43 (br), 5.28 (br), 5.08 (br). IR (KBr, cm^{-1}): 3409 (NH), 1611 (C═N), 1579 (phenyl), 1511, 957, 695. MALDI-TOF-MS: calcd 5458.7 $[M]^+$, found 5458.2, 2674.9, which is a fragment peak based on the cleavage of the C−N single bond in the first shell (calcd 2675.3).

Shell-Selective Reduction of Imines in DPA-F G2. To the dichloromethane/acetonitrile (1:1) solution (100 mL) of DPA-F G2 (100 mg, 8.16×10^{-5} mol) and $SnCl_2$ (62 mg, 3.27×10^{-4} mol), $NaBH_4$ (24 mg, 6.5×10^{-4} mol) was added. The reaction mixture was stirred at room temperature for 10 min. After the reaction, the crude mixture was washed with water including 1% triethylamine (four times), and the organic layer was dried using Na_2SO_4. DPA-F G2 having four amines at the second shell (DPA-F-red G2, 80% NMR yield) was formed as a main product. The separation of DPA-F-red G2 from the crude products was quite difficult due to the very small difference of the R_f values, but DPA-F-red G2 (20 mg) was isolated by silica gel column chromatography (5:1:1 hexane:chloroform:ethyl acetate). DPA-F-red G2: ^{1}H NMR (400 MHz, $CDCl_3$, TMS standard, ppm): δ 7.53 (d, $J = 8.3$ Hz, 4H), 7.35−7.22 (m, 40H), 6.82 (d, $J = 8.3$ Hz, 4H), 6.48 (d, $J = 8.3$ Hz, 4H), 6.27 (d, $J = 8.3$ Hz, 4H), 5.57 (d, $J = 4.4$ Hz, 2H), 5.48 (d, $J = 4.4$ Hz, 2H), 4.60 (d, $J = 4.4$ Hz, 2H), 4.27 (d, $J = 4.4$ Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS standard, ppm): δ 175.77, 150.46, 148.57, 143.02, 142.74, 132.39, 130.30, 129.44, 128.92, 128.17, 128.10, 128.02, 126.27, 113.01, 112.91, 62.98, 62.83.

IR (KBr, cm^{-1}): 3410 (NH), 1604 (C═N), 1584 (phenyl), 1318, 1178, 700. MALDI-TOF-MS: calcd 1233.4 $[M]^+$, found 1233.6, 1065.5, which is a fragment peak based on the cleavage of the C−N single bond in the second shell (calcd 1066.2).

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