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Novel Phenylazomethine Dendrimers: Synthesis and Structural Properties

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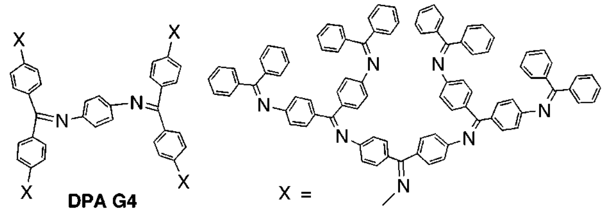
ABSTRACT



The novel dendrimers consisting of a π-conjugated backbone, the dendritic polyphenylazomethines (DPAs), were synthesized by the convergent method via the dehydration of aromatic ketones with aromatic amines in the presence of titanium(IV) tetrachloride. The obtained DPAs have a high solubility unlike the conventional linear polyphenylazomethines. NMR studies revealed the conformational rigidity of DPA G4. DPAs having many azomethine groups as the coordination site for metal ions are expected to be novel ligands.

Metal-ion collecting and/or endohedral metallodendrimers are expected as novel nanomaterials for electronic devices or catalysts.[1] We synthesized these novel dendrimers with a π-conjugated backbone, i.e., the dendritic polyphenylazomethines (DPAs).[2] DPAs have a high solubility unlike the conventional linear polyphenylazomethines, and the conformational rigidity was confirmed by NMR. DPA provides the potential for metal-ion collecting and/or endohedral metallodendrimers based on the strong coordinating ability of the imine sites, in which metal ions are incorporated into the inner space of the DPA. These properties will be used to develop nano-ordered hybrid organometallic materials for electronic devices.

DPAs (DPA G1, G2, G3, and G4, designated as GX where X is the generation number) 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, which is a common dehydration agent.[3] The DPA dendron G2 was synthesized via dehydration 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.[4] 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 the dehydration of benzophenone, 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

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[1] (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.

[2] 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.

[3] Higuchi, M.; Yamamoto, K. *Org. Lett.* **1999**, *1*, 1881.

[4] The dendron G2 is easily removed from the side product arising by the reaction of two molecules of **1** by means of 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.

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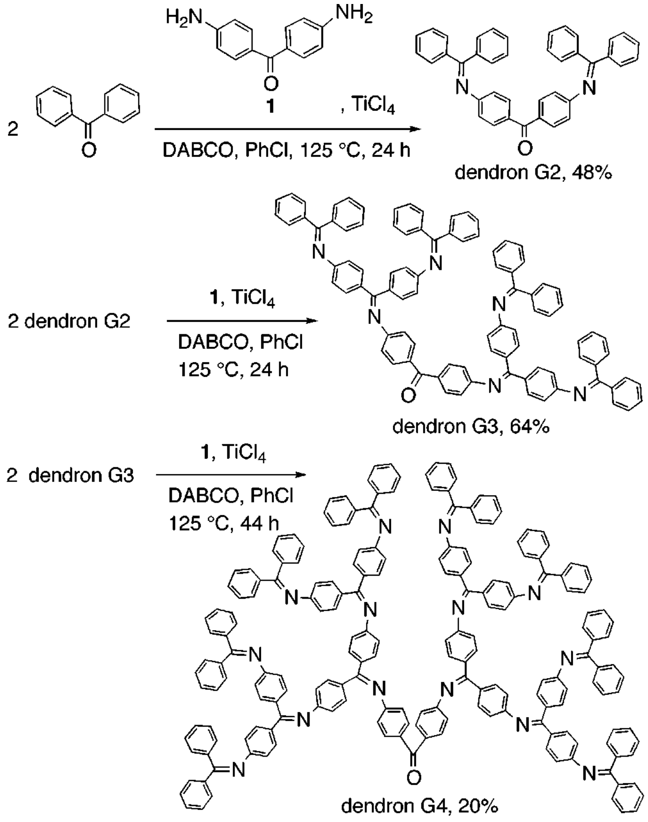
Scheme 1 Convergent Synthesis of the DPA Dendrons



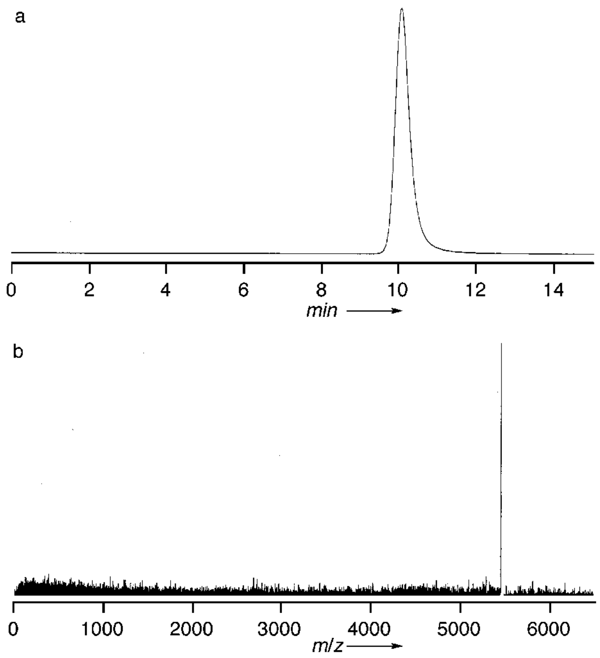


Figure 1. (a) GPC trace of DPA G4 ($M_w/M_n = 1.02$). (b) MALDI-TOF-MS spectrum of DPA G4 (calcd 5451.26 $[M + H]^+$, found 5451.48).

by MS, NMR, IR, and elemental analysis. The GPC analysis ($M_w/M_n = 1.02$) and 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.

Linear polyphenylazomethines have a very low solubility; therefore, structural studies have been difficult.[5] DPAs, on the other hand, have a high solubility in the common solvents such as chloroform and DMSO, because their dendritic structures prevent intermolecular stacking. 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 (Figures 2a, 2b, and 2c). This singlet peak supports the symmetrical structure of the DPA. On the other hand, the singlet peak was not observed in the spectrum of DPA G4 (Figure 2d). 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 3).

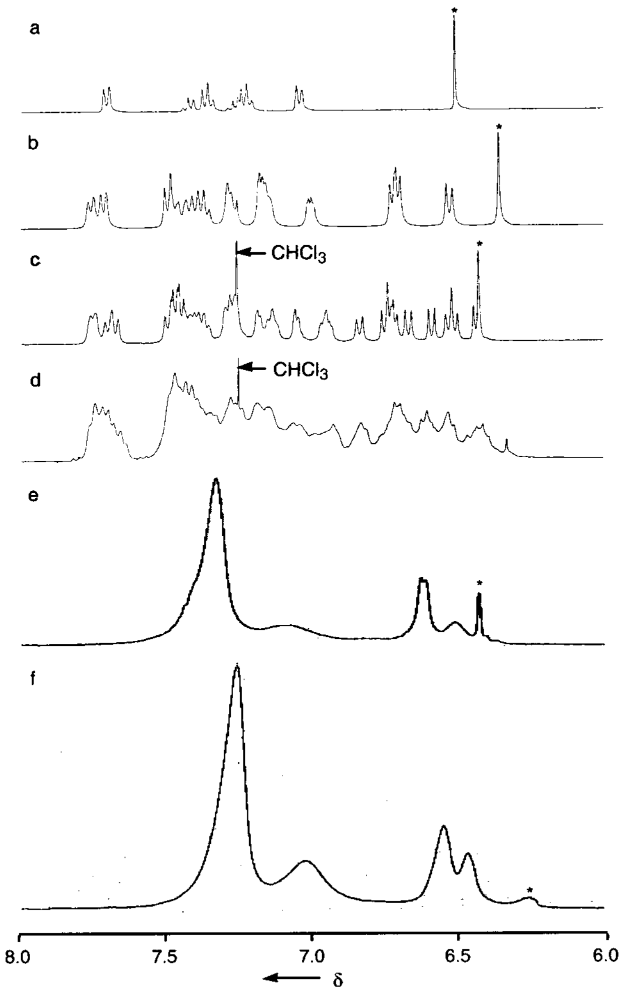
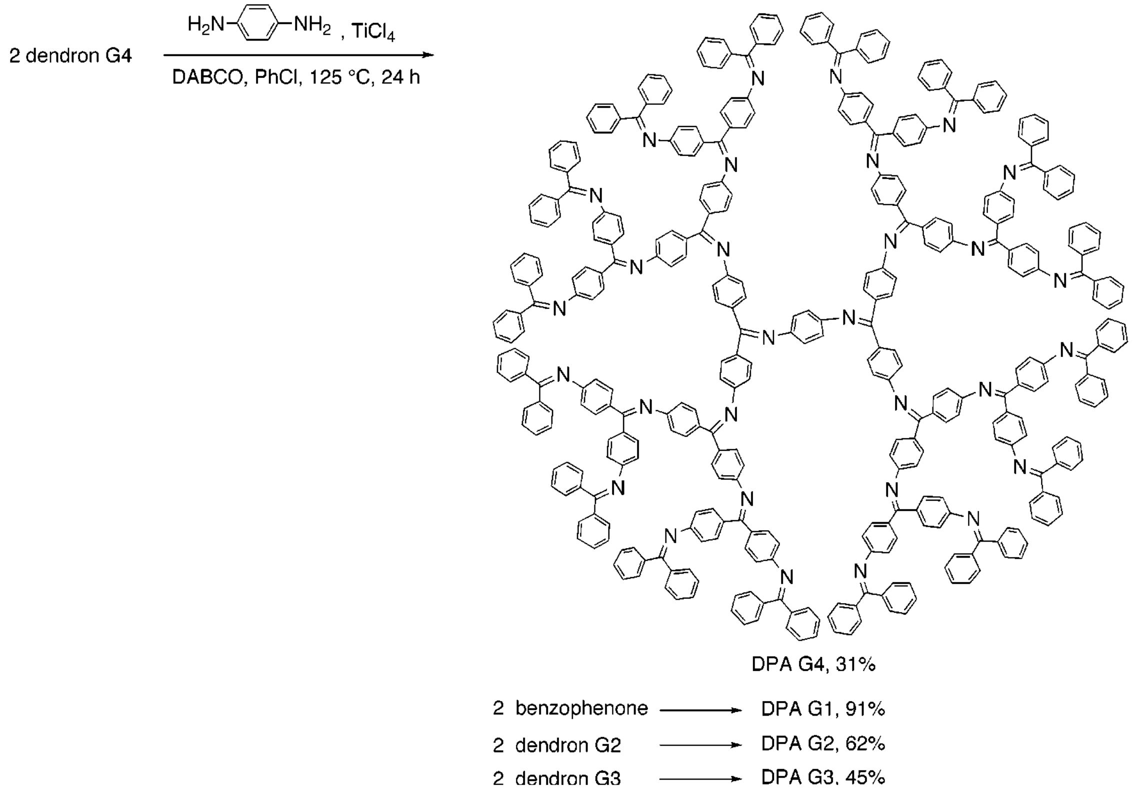


Figure 2. The ^{1}H NMR spectra of DPAs (a) G1, (b) G2, (c) G3, and (d) G4 in $CDCl_3$ at 30 °C and those of DPAs (e) G3 and (f) G4 in DMSO-d_6 at 130 °C. The marked peaks (*) are attributed to the four protons of the phenyl ring in the core of the DPAs.

Scheme 2. Synthesis of DPAs



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 2f). 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 2e).

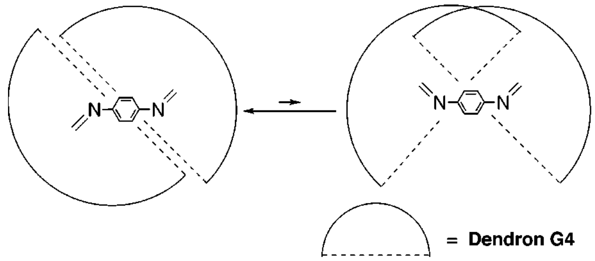


Figure 3. The fixed conformation in the core of DPA G4 by the bulky dendrons.

In Figure 2, 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, 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. These results are shown in Figure 4. The NMR studies for the relaxation gave useful information about the structural density.[6] With increasing generation, T_1 of the

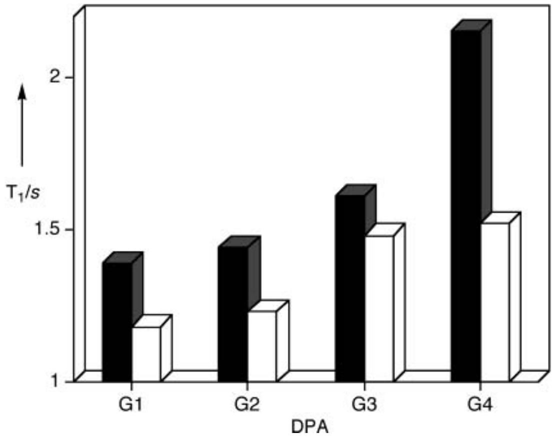


Figure 4. Spin–lattice (T_1) relaxation time of the external (black bars) and internal (white bars) protons in each generation of DPAs.

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(5) (a) Volpe, A. A.; Carson, J. C., Jr.; 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.

external proton increased more than that of the internal one. The increase in T_1 means a restriction in the molecular motion of the external phenyl rings; the exterior of DPA G4 is proposed to be close to the solid state.

DPAs are expected to be metal-ion collecting material based on the coordinating ability of the imine sites. The complexation of DPA with silver(I) ions was confirmed by ^{13}C NMR spectra (400 MHz, THF-d_8); the peaks attributed to the imine carbons of DPA G4 were shifted to a lower magnetic field by about 10 ppm due to the complexation, which is now being investigated in detail.[7]

In conclusion, the novel dendrimers consisting of the π-conjugated backbone, the dendritic polyphenylazomethines (DPAs), were synthesized by the convergent method via the dehydration of aromatic ketones with aromatic amines in the presence of titanium(IV) tetrachloride. The obtained DPAs have a high solubility, unlike the conventional linear polyphenylazomethines. The NMR studies revealed that the DPA G4 molecules have a rigid structure. DPAs having many azomethine groups as the coordination site for metal ions expand their application as a novel nano-ordered film of the DPA−metal complex.

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Supporting Information Available: Detailed experimental procedures and characterization data of DPA dendrons and dendrimers. This material is available free of charge via the Internet at http://pubs.acs.org.

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(6) (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.

[7] Ag(I) binding was also confirmed by IR measurement; an absorption of the imine bond in DPA G4 (1617 cm^{-1}) was shifted to 1624 cm^{-1} by complexation with Ag(I) ions.