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Efficient Synthesis of Poly(phenylazomethine) Dendrons Allowing Access to Higher Generation Dendrimers

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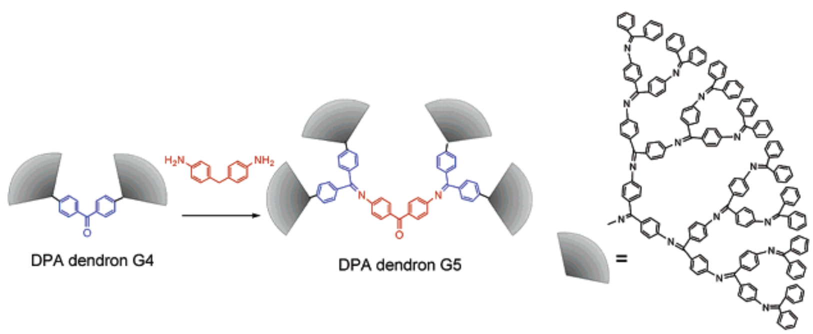
ABSTRACT



We have developed a novel synthetic method of phenylazomethine dendrons that uses 4,4′-methylenedianiline instead of 4,4′-diaminobenzophenone to synthesize the precursor of the phenylazomethine dendron and then oxidized the precursor to the next-generation dendron. For this method, the productivity of the dendrons has been significantly increased. Furthermore, as the synthesis of high-generation dendrons becomes easier, synthesis of DPA G5 was achieved.

Dendritic polyphenylazomethines (DPAs)[1,2] containing a C═N-conjugated backbone have a conformational rigidity, and their imine sites can trap metal ions. Particularly, the imines on DPA show a stepwise radial complexation with $SnCl_2$ from the core imines to the terminal imines based on the gradients in the basicity of the imine groups, which can be controlled by substituents on the core phenyl.[3] Due to these unique properties, DPAs are expected to be used as novel nanomaterials such as charge accumulation devices, photovoltaic devices, and environmental catalysts.[4,5] We revealed that DPA with a cobalt-porphyrin core acts an efficient catalyst for reduction of CO_2,[6] and organic light-emitting

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(3) (a) Yamamoto, K.; Higuchi, M.; Shiki, S.; Tsuruta, M.; Chiba, H. *Nature* **2002**, *415*, 509. (b) Enoki, O.; Imaoka, T.; Yamamoto, K. *Org. Lett.* **2003**, *5*, 2547.

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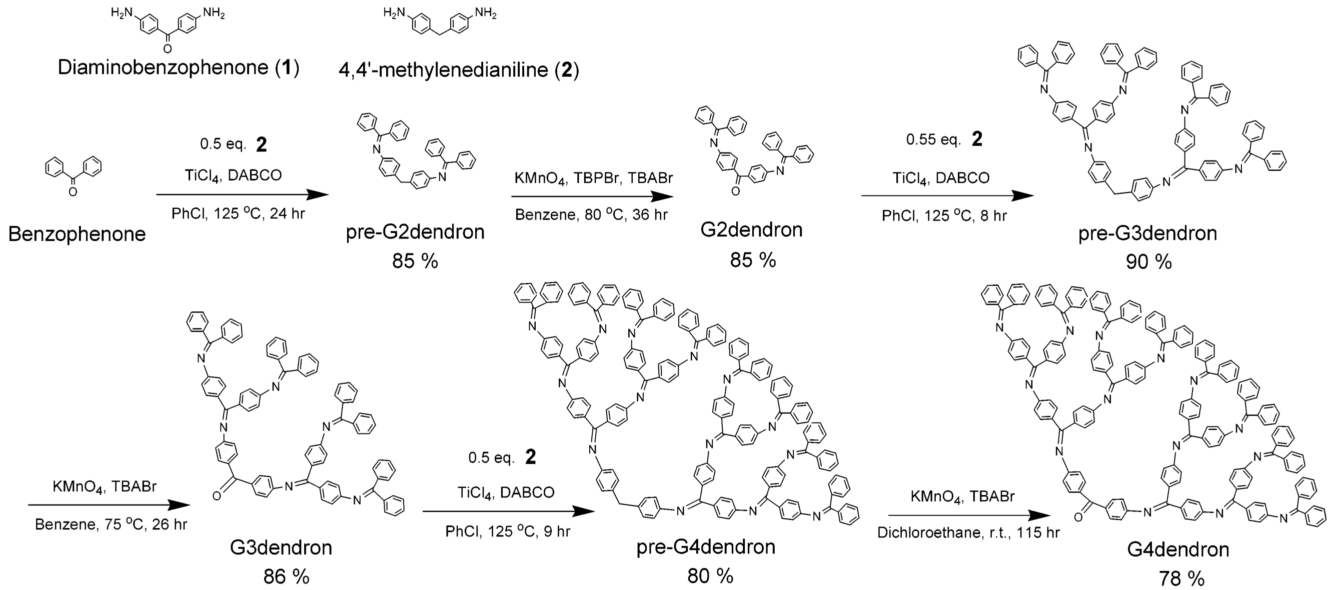
Scheme 1. New Synthetic Method of DPA Dendrons



diodes (OLEDs) using DPA with a triphenylamine core complexed with $SnCl_2$ as a hole-transport material show a significant EL performance improvement compared to non-metal-complexed ones.[7]

DPA has very interesting properties, but its synthesis is very difficult. Formerly, we synthesized DPA dendrons by the convergent method, using the dehydration of 4,4′-diaminobenzophenone (**1**) and the lower generation of the dendron (or benzophenone) in the presence of titanium(IV) tetrachloride.[4] But this reaction has the following two problems: first, undesired dehydrations arise because the 4,4′-diaminobenzophenone contains amines and a ketone. Second, this reaction requires an excess of dendron to prevent any undesired dehydrations. For such reasons, the yields are not good, and the synthesis of the higher generation dendron resulted in a lower yield, which makes it difficult to synthesize the fifth-generation dendrimer. Therefore, we developed a novel synthetic method to reduce such problems, and the yields underwent a significant improvement. Moreover, we achieved the synthesis of DPA G5. For the improved productivity of DPA dendrons by this novel method, the use of DPAs has increased.

The novel method is described as follows. Precursors of DPA dendrons (pre-DPA dendrons) were synthesized by dehydration of 4,4′-methylenedianiline (**2**) instead of 4,4′-diaminobenzophenone and DPA dendron (or benzophenone) in the presence of titanium(IV) tetrachloride. The oxidation of the benzyl methylene on the precursor to ketone by $KMnO_4$ then gave the DPA dendrons.[8] This method requires only a theoretical amount of the DPA dendron, because reaction occurs with no undesired dehydration. Therefore, all the dehydrations on each of the DPA dendrons had greater than 80% yields. The pre-DPA dendrons are efficiently oxidized by $KMnO_4$ with greater than 80% yield on each of the pre-DPA dendrons, because $KMnO_4$ is a base; therefore, the hydrolysis of the pre-DPA dendron hardly occurred and the phenylazomethine is very strong for oxidation. Consequently, this novel method allows remarkable progress in the synthesis of the DPA dendron.

The precursor of the DPA dendron G2 (pre-DPA dendron G2) was synthesized via dehydration of 4,4′-methylenedianiline and benzophenone with an 85% yield and then oxidized to the DPA dendron G2 by $KMnO_4$ with an 85% yield. Similarly, the pre-DPA dendron G3 and DPA dendron G3 were obtained with 90 and 86% yields, and the pre-DPA dendron G4 and DPA dendron G4 were obtained with 80 and 78% yields, respectively. The pre-DPA dendrons and DPA dendrons were isolated by silica gel chromatography, reprecipitation, or preparative-scale gel permeation chromatography (GPC). The pre-dendrons and dendrons were identified by MS, NMR, and TLC.

Table 1. Comparison between New and Conventional Method

	new method	conventional[a]
benzophenone	4.80 g	847 g
G2 dendron	5.15 g	121 g
G3 dendron	4.64 g	36.0 g
G4 dendron	3.10 g	3.10 g
G4 dendrimer	1.00 g	1.00 g

[a] For detailed conditions and yield of the conventional method, see ref 2.

(7) Satoh, N.; Cho, J.-S.; Higuchi, M.; Yamamoto, K. *J. Am. Chem. Soc.* **2003**, *125*, 8104.

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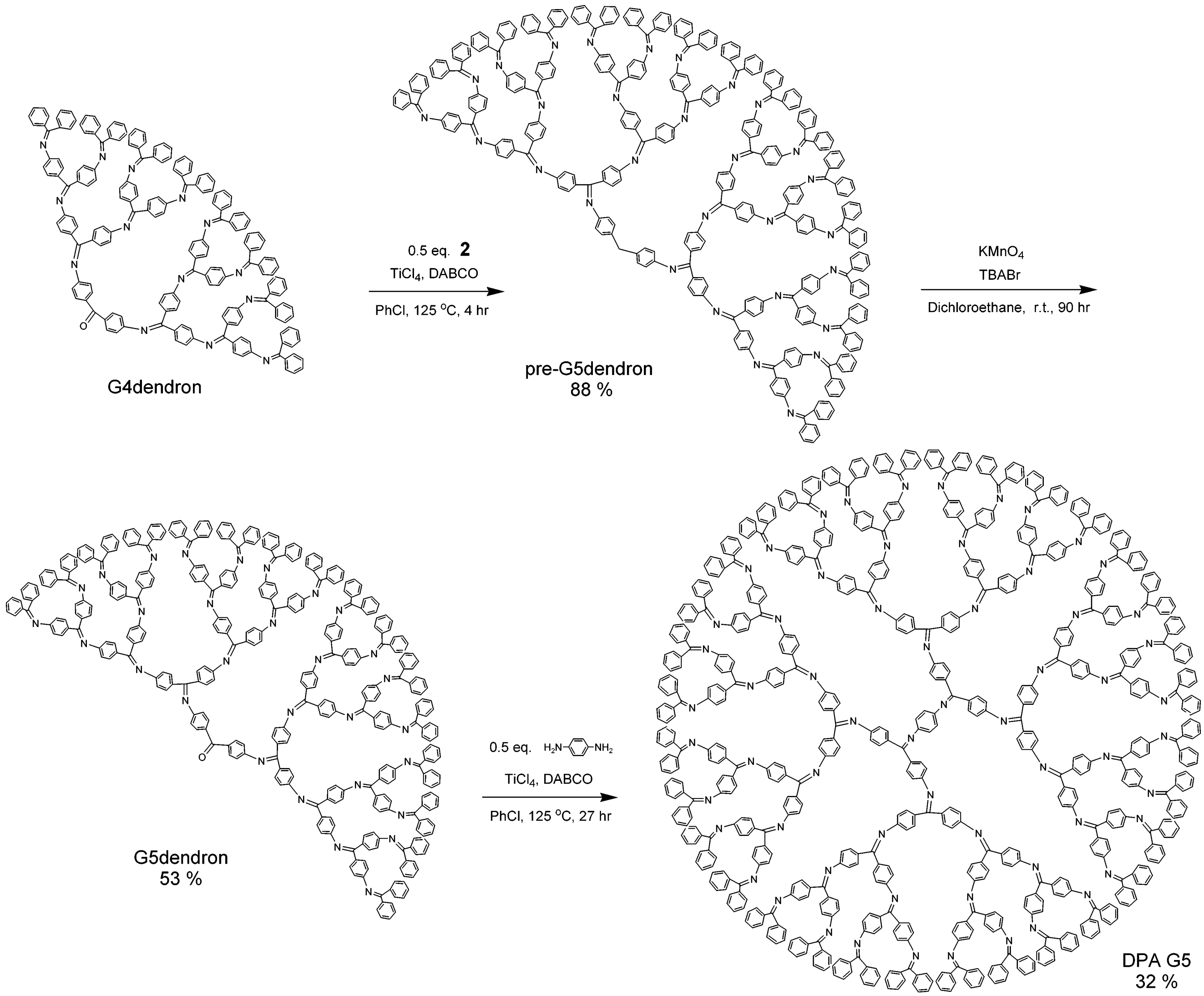
Scheme 2. Synthesis of DPA G5 via New Method



To compare with the conventional synthesis, the weight of the benzophenone and dendrons required to obtain 1 g of DPA G4 are shown in Table 1. As can be seen in Table 1, the novel method achieved a great reduction in the raw material; for example, the amount of the benzophenone required to obtain 1 g of DPA G4 becomes 1/176. Furthermore, a higher generation of the dendron occurs, thus producing a higher synthesis efficiency; therefore, this novel synthetic method is more available than the conventional method, particularly for high-generation dendrons.

Formerly, because the yield of the high-generation dendron was very low, the generation limit was four, and a higher generation did not occur. With this newly developed method, the syntheses of DPA dendron G5 and DPA G5 were achieved. In the same way as the lower generation dendrons, the pre-DPA dendron G5 was obtained by the dehydration of 4,4′-methylenedianiline and the DPA dendron G4 in the presence of titanium(IV) tetrachloride with an 88% yield and then oxidized to the DPA dendron G5 by $KMnO_4$ with a 53% yield. DPA G5 was synthesized via dehydration of *p*-phenylenediamine and the DPA dendron G5 with a 32% yield. The products were isolated by silica gel chromatography and preparative-scale GPC. The isolated pre-DPA dendron G5 and DPA dendron G5 were identified by MS, NMR, and TLC, and DPA G5 was identified by MS, NMR, and triple-detector[9] SEC (size exclusion chromatography). The triple-detector SEC data ($M_w/M_n = 1.01$) and MALDI-TOF-MS spectrum of DPA G5 are shown in Figure 1.

In conclusion, we have developed a novel synthetic method of phenylazomethine dendrons that uses 4,4′-methylenedianiline instead of 4,4′-diaminobenzophenone to synthesize the precursor of the phenylazomethine dendron and then oxidized the precursor to the next-generation dendron. This method significantly increased the productivity of the den-

(9) System is equipped with refractive index, viscosity, and light scattering detectors.

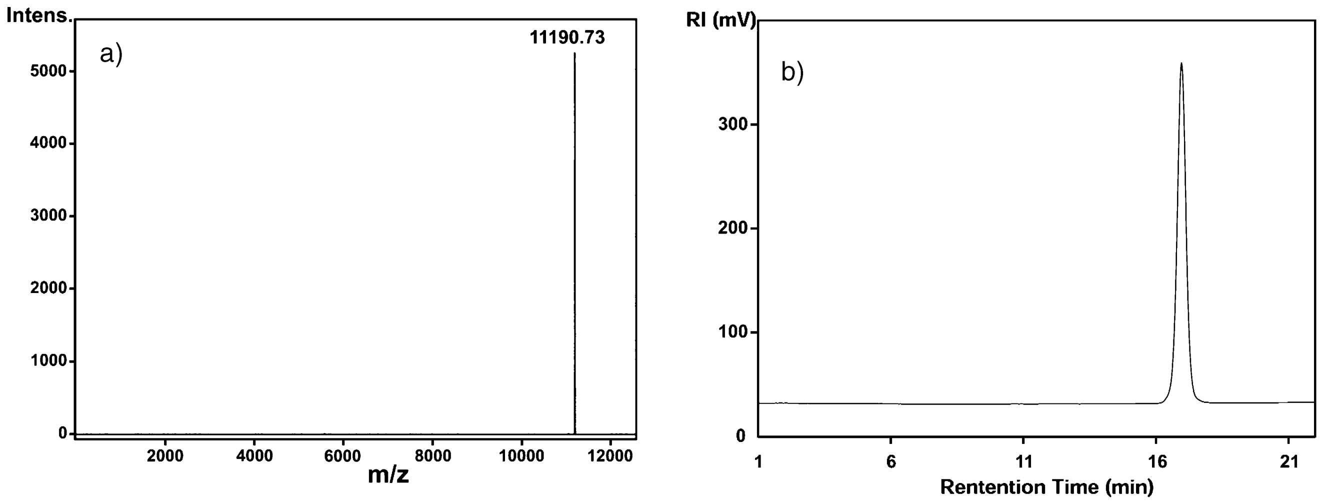


Figure 1. (a) MALDI-TOF MS spectrum of DPA G5 (calcd 11190.58 $[M + H]^+$, found 11190.73). (b) Triple-detector SEC data of DPA G5 monitored by RI ($M_w/M_n = 1.01$, $M_w = 11\,200$).

drons. Furthermore, as the synthesis of high-generation dendrons becomes easier, the synthesis of DPA G5 was achieved. We intend to study the properties of DPA G5, especially its metal-assembling property.

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Supporting Information Available: Detailed experimental procedures and characterization data of pre-DPA dendrons and DPA G5. This material is available free of charge via the Internet at http://pubs.acs.org.

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