# The Synthesis and Properties of Carbazole−Phenylazomethine Double Layer-Type Dendrimers

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ABSTRACT: A new double layer-type dendrimer with carbazole as the outer layer and phenylazomethine as the inner layer of the dendron was synthesized using the Ullmann reaction and dehydration reaction in the presence of titanium tetrachloride. In this dendrimer, the carbazole units act as excellent hole-transporters, the phenylazomethine units act as metal assembling sites, and the combination of both units provides a thermally stable shell for which the 10% weight loss temperature was over 550 °C. The dendrimers were used as the hole-transporting layer in an OLED device. The OLED device performance increased when the generation of the carbazole increased, corresponding to the higher HOMO level. Additionally, the enhancement of the hole-transporting property was observed by simple complexation of the metal ions to the imine site. Next, the effect of the generation of phenylazomethine was observed and compared to the asymmetric-type carbazole-phenylazomethine dendrimers. When the generation of phenylazomethine increased in the asymmetric-type dendrimer, the device performance decreased. In contrast, the performance did not change using the double layer-type dendrimer. This indicates that the outer layer carbazole works as a hole-transporting shell, and the double layer-type architecture is an ideal structure.

## Introduction

Because of the unique structure, definite molecular weight, and interesting functions, dendrimers have been the focus of constant attention.[1] Dendrimers are generally constructed with three main parts, i.e., the core, dendron, and periphery, which allow the design of novel multifunctional molecules. Previously, several dendritic architectures were created to allocate functional groups to a definite position of the molecule. For example, core or terminal modified,[2] layered,[3] segmented,[2a,3a,4] and tailored[5] type dendrimers have been reported. However, the relation between the architecture and the function is not clear, because synthesizing two or more dendritic architectures with the same functional groups is difficult.

Along with the progress in organic electronics, several low molecular,[5] high molecular (polymer),[6] and dendritic[7] materials were developed. The unique characteristic of dendritic materials is the definite and high molecular weight, which allows an amorphous and homogeneous film to be generated by a solution process. In addition to this, the dendritic structure allows for increase in the glass transition temperature, isolation of chromophores, reducing concentration quenching, and harvesting light with the dendrons.[9] These functions are difficult to attain with the usual molecular architecture. Therefore, dendritic materials are presumed as the next generation organic electronic material.

Typically, carbazole derivatives[10,11] are common functional groups well-known for their unique photo- and electrochemistries[12] and for their practical use as photo sensitizers[13] or a hole-transporting materials.[14] The dendritic phenylazomethines are also known as hole-transporting materials[15] and as coordination sites of metal ions.[16] The characteristic point of this unit is that the hole-transporting property will be enhanced by coordination of the metal ions.[15] Recently, we reported an asymmetric type carbazole−phenylazomethine dendrimer.[11a] In this dendrimer, the high hole-transporting property of the carbazole units and the enhancement of it by metal coordination to the phenylazomethine group were compatible. However, in this dendrimer, both functional groups were at the surface of the dendrimer, but the hole-transporting property and the thermal stability of the carbazole is essentially higher than the phenylazomethine. Therefore, the double layer-type architecture that has carbazole as the outer layer and phenylazomethine as the inner layer should be an ideal architecture, and the comparison of the asymmetric- and layer-type dendrimer is an interesting subject. We now report the synthesis and properties of the carbazole−phenylazomethine double layer-type dendrimer with a porphyrin core and compare the hole-transporting property with the asymmetric-type carbazole−phenylazomethine dendrimer[11a] to clarify the relation of the architecture and the function.

## Experimental Section

Carbazole was purchased from the Kanto Kagaku Co. and recrystallized once before use. All other reagents were purchased from Aldrich, TCI, and Kanto Kagaku Co. and used without further purification. The NMR spectra were obtained using a JEOL JNM-GX400 (400 MHz) and a JEOL JNM-EX270 (270 MHz) with TMS as the internal standard. The MALDI TOF-MS data were obtained using a KOMPACT MALDI mass spectrometer (Shimadzu/Kratos) or Shimadzu/Kratos AXIMA CFR plus in the positive ion mode. Dithranol was used as the matrix. The elemental analysis was performed at the Central Service Facilities for Research of Keio University. A preparative scale gel permeation chromatograph, LC-908 (Japan Analytical Industry Co., Ltd.), was used to isolate each compound with chloroform or THF as the solvent. The thermal analysis was performed using a Rigaku Thermoplus TG8120 with flowing nitrogen, and the rate of temperature increase was 40 K/min for the temperature vs weight loss measurements. The UV−vis spectra were recorded using a Shimadzu UV-3150 spectrometer with a quartz cell having a 1 cm optical length. The electrochemical measurements were done by a conventional three-electrode

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configuration using an ALS Chi660 electrochemical analyzer. The working electrode was a GC electrode. The counter and the reference electrodes were Pt wire and $Ag/Ag^+$, respectively. The solvent was 1,2-dichloroethane, the concentration of the sample was 0.5 mM, and the supporting electrolyte was 0.2 M tetra-*n*-butylammonium perchlorate. The increased voltage was 0.004 V, the amplitude was 0.05 V, the pulse width was 0.06 s, the sample width was 0.02 s, and the pulse period was 0.2 s for DPV measurements. Analytical size-exclusion chromatography (SEC) was performed using an HPLC (Shimadzu, LC-10AP) equipped with a TSK-GEL CMHXL (Tosoh) at 40 °C. Tetrahydrofuran (THF) was used as the eluent at the flow rate of 1 mL/min. The detection line was connected to a triple detector (Viscotek, TriSEC model 302).

Conventional OLED devices having the ITO/dendrimer/$Alq_3$/CsF/Al structure were fabricated by spin coating the dendrimer (or dendrimer complex) solutions in chlorobenzene on an UV ozone treated ITO-coated glass anode. $Alq_3$ (50 nm), CsF (2 nm), and Al (100 nm) were successively vacuum-deposited on top of the hole-transporting layer. The emitting area was 9 $mm^2$. The current vs voltage characteristics were measured using an Advantest R6243 current/voltage unit. Luminance was measured by a Minolta LS-100 luminance meter in air at room temperature. The dendrimer complex was prepared by the following method. To a solution of the dendrimer in chloroform was added a solution of $SnCl_2$ in acetonitrile and evaporated to dryness to give the dendrimer complex.

**CzG2on (5).** The carbazole G2 dendron (**5**) was obtained according to the literature method. See reference 11a.

**4,4′-Diiodobenzophenone (2).** The 4,4′-diiodobenzophenone (**2**) was obtained according to the literature method. See reference 17.

**G1-1on (General Procedure for Ullmann Reaction).** A mixture of carbazole (730 mg, 4.39 mmol), 4,4′-diiodobenzophenone **2** (871 mg, 2.01 mmol), and copper(I) oxide (880 mg, 6.15mmol) in *N*,*N*-dimethylacetamide (DMAc) (20 mL) was heated in an oil bath at 165 °C for 48 h under a nitrogen atmosphere. The reaction mixture was cooled to room temperature and then filtered through Celite. The filtrate was concentrated, and the product was isolated by silica gel column chromatography (hexane:ethyl acetate = 10:1) and then purified using preparative GPC (eluent: chloroform). Yield: 83% (851 mg, 1.66 mmol). $^1H$ NMR (270 MHz, $CDCl_3$, 22 °C, ppm): 8.17 (d, $J = 1.9$ Hz, 4H), 8.14 (s, 4H), 7.78 (d, $J = 8.9$ Hz, 4H), 7.55 (d, $J = 8.1$ Hz, 4H), 7.45 (t, $J = 7.0$ Hz, 4H), 7.32 (t, $J = 7.6$ Hz, 4H) (see Figures S3 and S4). $^{13}C$ NMR (100 MHz, $CDCl_3$, 24 °C, ppm): 194.28, 141.78, 140.14, 135.70, 131.76, 126.32, 126.16, 123.80, 120.59, 120.43 109.73 (see Figure S5). MALDI TOF-MS (matrix: dithranol): $[M+H]^+$ calcd, 513.2; found, 513.4. Anal. Calcd for $C_{37}H_{24}N_2O$: C, 86.69; H, 4.72; N, 5.46. Found: C, 86.52; H, 4.81; N, 5.30.

**G1-2on**. As per the general procedure for the Ullmann reaction, CzG2on **5** (481 mg, 0.97mmol), 4,4′-diiodobenzophenone **2** (190 mg, 0.44 mmol), and copper(I) oxide (200 mg, 1.40 mmol) in *N*,*N*-dimethylacetamide (DMAc) (7.5 mL) was heated in an oil bath at 165 °C for 31 h under a nitrogen atmosphere. Isolation by silica gel column chromatography (hexane:ethyl acetate = 4:1) and purification using preparative GPC (eluent: chloroform) gave **G1−2on** (238 mg, 0.20mmol) in 46% yield. $^1H$ NMR (270 MHz, $CDCl_3$, 21 °C, ppm): $\delta$ 8.31 (dd, $J = 1.4, 3.5$ Hz, 8H), 8.15 (d, $J = 7.6$ Hz, 8H), 7.98 (d, $J = 8.6$ Hz, 4H), 7.81 (d, $J = 8.6$ Hz, 4H), 7.67 (dd, $J = 1.9, 8.9$ Hz, 4H), 7.40 (d, $J = 3.8$ Hz, 16H), 7.28 (m, 8H) (see Figures S6 and S7). $^{13}C$ NMR (68 MHz, $CDCl_3$, 23 °C, ppm): $\delta$ 193.94, 141.53, 141.23, 139.89, 136.31, 132.08, 130.00, 126.61, 126.44, 125.85, 124.45, 123.13, 120.28, 119.83, 119.73, 111.24, 109.53 (see Figure S8). MALDI TOF-MS (matrix: dithranol): $[M+H]^+$ calcd, 1173.4; found, 1172.5. Anal. Calcd for $C_{85}H_{52}N_6O$: C, 87.01; H, 4.47; N, 7.16. Found: C, 86.61; H, 4.68; N, 6.91.

**Pre-G2-2on. G1-2on** (1480 mg, 1.26 mmol), methylenedianiline **6** (121 mg, 0.61 mmol), and 1,4-diazabicyclo[2. 2. 2]octane (DABCO) (808 mg, 7.20mmol) were dissolved in chlorobenzene (20 mL) and heated to 60 °C. $TiCl_4$ (200 mg, 1.80 mmol) dissolved in 3 mL of chlorobenzene was added dropwise, and the addition funnel was then rinsed with 3 mL of chlorobenzene. The mixture was then heated to 125 °C and stirred for 3.5 h under a nitrogen atmosphere. The reaction mixture was cooled to room temperature and stirred for 4 h in air. Then few drops of $Et_3N$ were added and filtered through silica gel. The filtrate was concentrated, and the product was isolated by preparative GPC (eluent: chloroform). Yield: 96% (1460 mg, 0.58 mmol). $^1H$ NMR (400 MHz, $C_4D_8O$, 19.7 °C, ppm): $\delta$ 8.49 (d, $J = 7.6$ Hz, 8H), 8.11 (dd, $J = 8.0, 15.6$ Hz, 16H), 7.99 (dd, $J = 8.0, 140$, 8H), 7.74 (dd, $J = 8.8, 42$ Hz, 8H), 7.66 (m, 16H), 7.46 (d, $J = 8.4$, 4H), 7.28 (m, 32H), 7.11 (m, 16H), 6.74 (d, $J = 8$, 4H), 3.88(s, 2H) (see Figures S9 and S10). $^{13}C$ NMR (100 MHz, $C_4D_8O$, 22.7 °C, ppm): $\delta$ 166.47, 150.15, 142.51, 141.09, 141.03, 140.22, 139.26, 137.45, 136.79, 132.15, 131.70, 131.61, 131.56, 129.62, 127.31, 127.19, 126.93, 126.42, 125.22, 124.01, 121.84, 120.79, 120.33, 111.89, 110.26, 41.21 (see Figure S11). MALDI TOF-MS (matrix: dithranol): $[M+H]^+$ calcd, 2509.9; found, 2509.0.

**G2-2on. PreG2-2on** (1210 mg, 0.48 mmol) and TBABr (1170 mg, 3.63 mmol) were dissolved in 1,2-dichloroethane (12 mL). $KMnO_4$ (610 mg, 3.86mmol) was then added to the solution and stirred for 48 h at room temperature. The reaction was quenched with aqueous sodium bisulfite. The organic layer was washed with water and brine, then dried over sodium sulfite, and concentrated. Isolation by silica gel column chromatography (hexane:toluene= 1:4 with 2% $Et_3N$) and purification using preparative GPC (eluent: chloroform) gave **G2-2on** (1000 mg, 0.40mmol) in an 83% yield. $^1H$ NMR (270 MHz, $C_4D_8O$, 21.6 °C, ppm): $\delta$ 8.30 *(*$J = 16.7, 99.9$ Hz, 16H), 8.13 (dd, $J = 8.4, 78.3$ Hz, 8H), 8.12 (s, 8H), 7.81 (dd, $J = 8.91, 35.1$ Hz, 8H), 7.66 (m, 16H), 7.48 (d, $J = 8.1$, 4H), 7.34 (m, 32H), 7.18 (m, 16H), 6.92 (d, $J = 8.37$, 4H) (see Figures S12 and S13). $^{13}C$ NMR (100 MHz, $C_4D_8O$, 22.7 °C, ppm): $\delta$ 193.59, 167.40, 155.84, 142.45, 141.00, 140.69, 138.50, 136.03, 133.83, 131.98, 131.70, 131.51, 131.37, 127.29, 126.93, 126.90, 125.31, 123.97, 121.01, 120.74, 120.30, 111.92, 110.21 (see Figure S14). TOF-MS: 2522.9 $[M+1]^+$. MALDI TOF-MS (matrix: dithranol): $[M+H]^+$ calcd, 2522.9; found, 2522.9. Anal. Calcd for $C_{183}H_{112}N_{14}O$: C, 87.12; H, 4.47; N, 7.77. Found: C, 86.20; H, 4.52; N, 7.57.

**ZnPG1-1 (General Procedure for Double Layer-Type Dendrimer).** [5,10,15,10-tetrakis(4-aminophenyl)-21H,23H-porphynato]-zinc(II) **7** (115 mg, 0.16 mmol), **G1-1on** (515 mg, 1.01 mmol), and DABCO (555 mg, 4.95 mmol) were dissolved in chlorobenzene (30 mL) and heated to 75 °C. $TiCl_4$ (223 mg, 1.17 mmol) dissolved in 5 mL of chlorobenzene was added dropwise, and the addition funnel was then rinsed with 5 mL of chlorobenzene. The mixture was heated to 125 °C and stirred for 1 h under a nitrogen atmosphere. The reaction mixture was cooled to room temperature and stirred overnight in air and then filtered through Celite. The filtrate was concentrated, and the product was isolated by silica gel column chromatography (toluene with 2% $Et_3N$) and purified by preparative GPC (eluent: THF). Yield: 20% (63 mg, 0.02 mmol). $^1H$ NMR (400 MHz, $C_4D_8O$, 23 °C, ppm): $\delta$ 8.74 (s, 8H), 8.31 (d, $J = 8.0$ Hz, 8H), 8.13 (d, $J = 6.4$ Hz, 16H), 7.86 (d, $J = 7.2$ Hz, 8H), 7.81 (d,

$J$ = 8.0 Hz, 8H), 7.57 (d, $J$ = 8.4 Hz, 8H), 7.41 (d, $J$ = 6.4 Hz, 16H), 7.25 (m, 40H), 7.01 (d, $J$ = 7.2 Hz, 8H) (see Figures S15 and S16). $^{13}$C NMR (100 MHz, $C_4H_8O$, 23 °C, ppm): $\delta$ 167.05, 151.24, 150.15, 140.52, 140.31, 138.47 137.92, 137.82, 135.26, 134.15, 131.29, 130.98, 126.39, 126.15, 125.96, 123.86, 123.62, 120.25, 120.19, 118.65, 109.73, 109.59 (see Figure S17). MALDI TOF-MS (matrix: dithranol): $[M+H]^+$ calcd, 2715.9; found, 2715.4.

**ZnPG1-2.** As per the general procedure for the dendrimer, [5,10,15,10-tetrakis(4-aminophenyl)-21H,23H- porphynato]-zinc(II) **7** (58 mg, 0.08mmol), **G1-2on** (556 mg, 0.47mmol), and DABCO (354 mg, 3.16mmol) were dissolved in chlorobenzene (20 mL). $TiCl_4$ (126 mg, 0.67 mmol) was added and the mixture was stirred for 2 h at 125 °C. The product was isolated by silica gel column chromatography (hexane: toluene = 1:4 with 2% $Et_3N$) and purified by preparative GPC (eluent: THF). Yield: 32% (136 mg, 0.03 mmol). $^1$H NMR (270 MHz, $C_4D_8O$, 22 °C, ppm): $\delta$ 8.68 (s, 8H), 8.58 (s, 16H), 8.33(d, $J$=8.1 Hz, 8H), 8.17(d, $J$=7.6 Hz, 16H), 8.02(m, 32H), 7.80(br, 24H), 7.63(t, $J$=8.6 Hz,16H), 7.54(d, $J$=8.4 Hz, 8H), 7.40(m, 32H), 7.24(t, $J$ = 7.5, 32H), 7.05 (m, 32H), 6.58 (d, $J$ = 7.6, 8H) (see Figures S18 and S19). $^{13}$C NMR (100 MHz, $C_4D_8O$, 19 °C, ppm): 167.01, 151.57, 150.82, 142.54, 142.16, 141.13, 140.89, 140.36, 139.10, 139.03, 138.24, 136.66, 134.55, 132.50, 132.04, 131.70, 131.65, 127.25, 127.04, 126.56, 126.42, 125.45, 215.41, 124.05, 120.99, 120.79, 120.39, 120.32, 119.27, 112.12, 111.96, 110.29, 110.20 (see Figure S20). MALDI-TOF-MS (matrix: dithranol): $[M+H]^+$ calcd, 5357.9; found, 5355.7.

**ZnPG2-2.** As per the general procedure for the dendrimer, [5,10,15,10-tetrakis(4-aminophenyl)-21H,23H-porphynato]-zinc(II) **7** (41.6 mg, 0.056mmol), **G2-2on** (701 mg, 0.28 mmol), and DABCO (551 mg, 4.89 mmol) were dissolved in chlorobenzene (10 mL). $TiCl_4$ (209 mg, 1.1 mmol) was added and the mixture was stirred for 2 h at 125 °C. The product was isolated by silica gel column chromatography (toluene with 2% $Et_3N$) and purified by preparative GPC (eluent: THF). Yield: 32% (192 mg, 0.018 mmol). $^1$H NMR (400 MHz, $C_4D_8O$, 18.5 °C, ppm): $\delta$ 8.81 (s, 8H), 8.51 (s, 16H), 8.43 (d, $J$ = 15, 16H), 8.20 (m, 32H), 7.99 (m, 64H), 7.86 (m, 16H), 7.66 (m, 64H), 7.37 (m, 192H), 7.08 (m, 48H), 6.94 (d, $J$ = 7.8, 8H), 6.60 (d, $J$ = 8.1, 8H) (see Figures S21 and S22). $^{13}$C NMR (100 MHz, $C_4D_8O$, 21.0 °C, ppm): $\delta$ 167.35, 154.19, 152.75, 152.28, 150.78, 142.40, 140.90, 140.48, 138.88, 138.56, 138.16, 136.25, 135.63, 132.47, 131.58, 131.22, 130.52, 127.30, 126.97, 126.42, 125.26, 123.97, 120.77, 120.32, 119.76, 111.85, 110.24 (see Figure S23). MALDI-TOF-MS (matrix: dithranol): $[M+H]^+$ calcd, 10753.8; found, 10752.9.

**DPAG2on and DPAG3on.** The compounds **DPAG2on** and **DPAG3on** were obtained according to the literature method. See reference 18.

**CzG2−NH$_2$, and asymmetric-type dendrimer Cz2−DPA2.** The compounds **CzG2−NH$_2$** and **Cz2−DPA2** were obtained according to the literature method. See reference 11a.

**Cz2−DPA1 (General Procedure for Asymmetric Dendrimer). Cz2−NH2**(250 mg, 0.425 mmol), benzophenone(76 mg, 0.414 mmol), and DABCO (204 mg, 1.83 mmol) were dissolved in chlorobenzene and heated to 75 °C. $TiCl_4$ (173 mg, 0.912 mmol) dissolved in chlorobenzene was added dropwise, and the addition funnel was then rinsed with chlorobenzene. The mixture was heated to 125 °C and stirred for 4 h under a nitrogen atmosphere. The reaction mixture was cooled to room temperature and stirred overnight in air and then filtered through Celite. The filtrate was concentrated, and the product was isolated by silica gel column chromatography (hexane:ethyl acetate:chloroform = 8:1:2 with 2% $Et_3N$) and purified by preparative GPC (eluent: THF). Yield: 86% (266 mg, 0.35 mmol). $^1$H NMR (400 MHz, $CDCl_3$, 20 °C, ppm): $\delta$ 8.25 (d, $J$ = 2.0 Hz, 2H), 8.16 (d, $J$ = 8.0 Hz, 4H), 7.85 (d, $J$=8.2 Hz, 2H), 7.59 (dd, 8.2, $J$=2.0 Hz, 2H), 7.54−7.45 (m, 8H), 7.42−7.37 (m, 12H), 7.30−7.25 (m, 4H), 7.04 (d, $J$=8.4 Hz, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$, 30 °C, ppm): $\delta$ 169.31, 151.31, 141.68, 140.79, 139.14, 135.90, 133.45, 131.80, 131.08, 130.05, 129.52, 129.40, 128.94, 128.28, 128.04, 127.42, 126.09, 125.79, 123.64, 123.05, 122.58, 120.20, 119.58, 111.16, 109.64. MALDI-TOF-Mass calcd, 752.3 $[M]^+$; found, 752.1. Anal. Calcd for $C_{55}H_{36}N_4$: C, 87.74; H, 4.82; N, 7.44. Found: C, 87.35; H, 4.94; N, 7.37.

**Cz2−DPA3.** As per the general procedure for the asymmetric dendrimer, **Cz2−DPA3** was synthesized using **Cz2−NH2** (185 mg, 0.314 mmol), **DPAG3on** (386 mg, 0.307 mmol), DABCO (204 mg, 1.83 mmol), and $TiCl_4$ (173 mg, 0.912 mmol) . The product was isolated by preparative GPC (eluent: THF). Yield: 97% (544 mg, 0.30 mmol). $^1$H NMR (400 MHz, $CDCl_3$, 20 °C, ppm): $\delta$ 8.24 (s, 2H), 8.16 (d, $J$ = 7.6 Hz, 4H), 7.77−6.53 (m, 84H). $^{13}$C NMR (100 MHz, $CDCl_3$, 20 °C, ppm): $\delta$ 168.77, 168.64, 168.36, 168.29, 168.08, 154.22, 153.76, 153.66, 152.28, 151.77, 151.73, 151.56, 141.49, 140.74, 139.01, 138.86, 138.62, 135.60, 135.52, 135.47, 133.96, 133.80, 133.63, 131.32, 130.80, 130.42, 130.30, 130.18, 130.11, 129.95, 129.81, 129.23, 129.17, 129.10, 128.61, 128.04, 127.87, 127.71, 127.63, 127.38, 125.92, 125.66, 123.47, 122.87, 120.78, 120.67, 120.56, 120.37, 120.15, 120.04, 119.91, 119.42, 111.14, 109.57. MALDI-TOF-Mass calcd, 1826.7 $[M]^+$; found 1826.3. Anal. Calcd for $C_{133}H_{90}N_{10}$: C, 87.38; H, 4.96; N, 7.66. Found: C, 87.00; H, 5.10; N, 7.51.

## Results and discussion

The strategy for the preparation of the carbazole-phenylazomethine layer-type dendron is outlined in Schemes 1 and 2. The carbazole G2 dendron[11a] and diiodobenzophenone **2**[17] were obtained according to the literature method. The **G1-1on** and **G1-2on** were synthesized by the classical Ullmann reaction between **2** and the carbazole dendrons in 83% and 46% yields (Scheme 1), respectively.

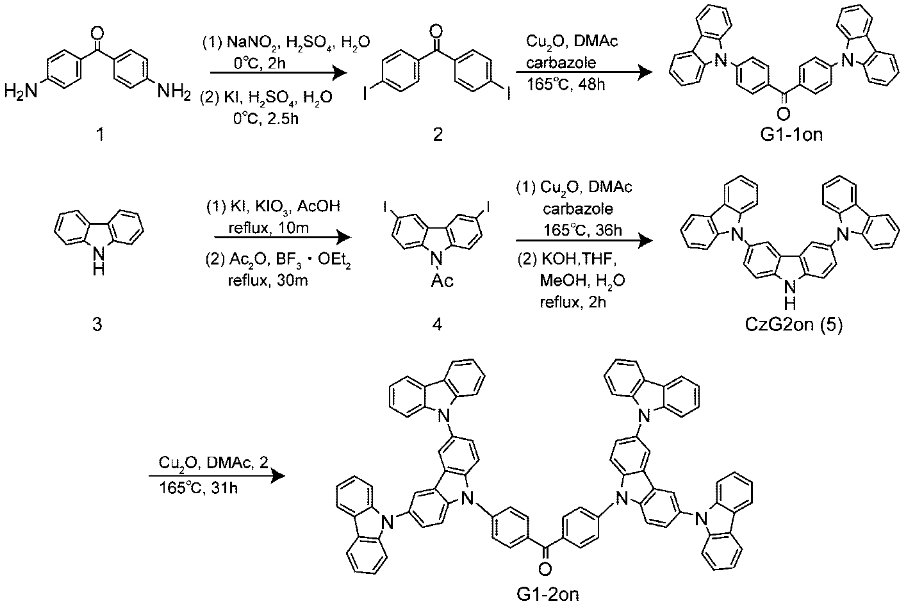
To add the phenylazomethine layer, the dehydration and oxidation reactions using $TiCl_4$ and $KMnO_4$ were used[18] for the **G1-2on**, and the **G2-2on** was obtained in an 80% yield (Scheme 2).

The double layer-type dendrimers were obtained by the dehydration reaction using $TiCl_4$ between the core compound [5,10,15,10-tetrakis(4-aminophenyl)-21H,23H-porphynato]-zinc(II) and the dendrons (Scheme 3).

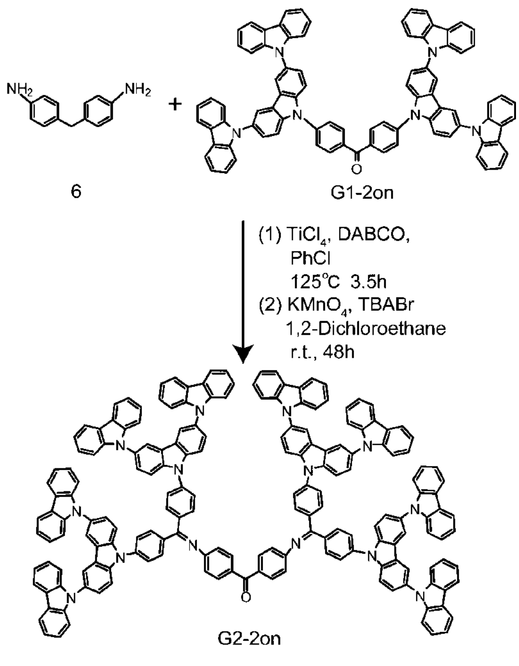
The recently reported strategy[11a] was used for the preparation of the asymmetric-type dendrimers. First, the amine substituted carbazole G2 dendron (**Cz2−NH$_2$**) was prepared, followed by the dehydration reaction using $TiCl_4$ with the corresponding dendritic phenylazomethine dendrons (Scheme 4). All products were identified by $^1$H NMR, $^{13}$C NMR, MALDI-TOF MS (Figure 1 and Supporting Information), and elemental analysis. Additionally, the purity of the double layer-type dendrimers were checked by HPLC (Figure 2).

The coordination chemistry of the dendrimer was confirmed by UV−vis titration with $SnCl_2$.[16] Upon the addition of $SnCl_2$ to the dendrimer solution (benzene:acetonitrile = 4:1), the spectra gradually changed (Figure 3), and the pattern was similar to the porphyrin core phenylazomethine dendrimers.[19] This means that the new dendrimers can assemble $SnCl_2$ at the imine sites. The equivalent amount of $SnCl_2$ per imine site that was needed for the spectral change to become saturated followed the order **ZnPG2-2** ≪ **ZnPG1-1** < **ZnPG1-2** (see Supporting Information), and the reverse sequence of this order directly reflects the difference in the binding constant. When the generation of the phenylazomethine layer increases, the com-

**Scheme 1. Synthesis of G1-1 and G1-2 Dendrons**



**Scheme 2. Synthesis of G2-2 Dendron**



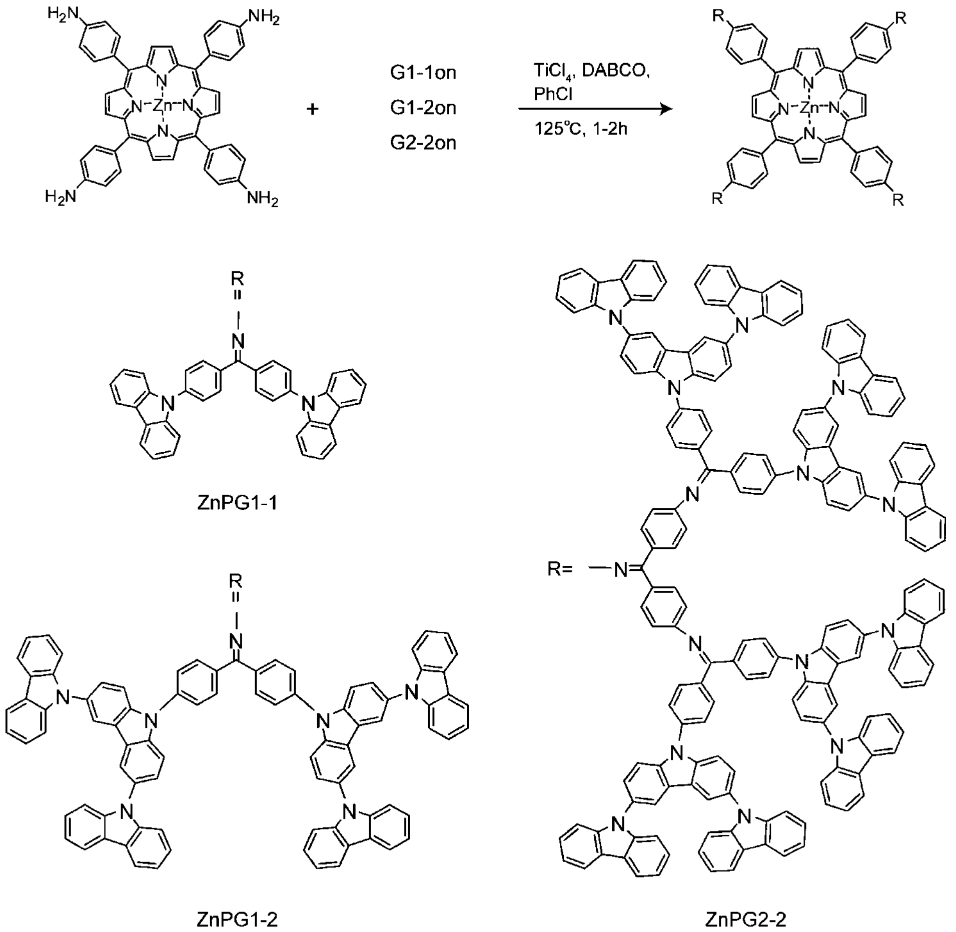
plexation property has an efficient increase, i.e., this shows that the dendritic structure and the electron donation from the outer phenylazomethine to the inner phenylazomethine increases the complexation property. This matches the result of the other phenylazomethine dendrimers.[19] On the other hand, when the generation of the carbazole increases, the complexation property has slightly decreased due to the substituent effect of the carbazole group.

The 10% weight loss temperatures ($Td_{10\%}$) of the double layer-type dendrimers were measured. The $Td_{10\%}$values of the dendrimers were 556 °C (**ZnPG1-1**), 667 °C (**ZnPG1-2**), and 603 °C (**ZnPG2-2**) (Figure 4). Interestingly, the $Td_{10\%}$were higher than the same generation phenylazomethine dendrimers (520−530 °C).[20] This indicates that the carbazole groups are thermally more stable than the phenylazomethine groups, and the outer layer carbazole works as a "shell" to enhance the thermal stability of the dendrimer.

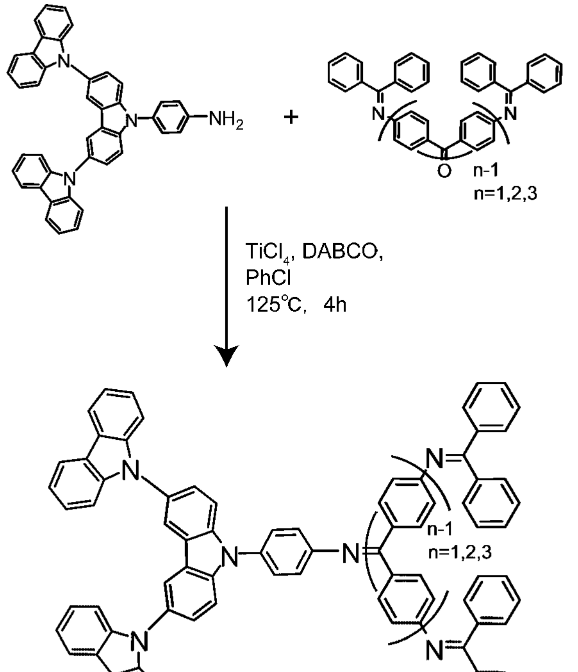
The electrochemical analysis of the double layer-type dendrimers were done using the DPV (differential pulse voltammetry) method (Figure 5). For **ZnPG1-1**, a peak at about 0.4 V (vs $Ag/Ag^+$) and 0.75 V followed by a large oxidation peak starting at about 0.8 V were observed, and for **ZnPG1-2** and **ZnPG2-2**, a peak at about 0.4 V followed by a large oxidation peak at about 0.7 V were observed. The peaks at about 0.4 V and 0.75 V are attributed to the first and second oxidations of zinc in the porphyrin,[19] respectively, and the large peak after them is attributed to the oxidation of the carbazole dendrons.[2b,11d,12] The oxidation peak of zinc became very weak in **ZnPG2-2** due to the common "dendritic shell effect".[15b,22] The HOMO of the double layer-type dendrimers are lying in the core. However, when dendrimers transport holes, the hole will hop through the peripheral groups. Therefore, the substantial HOMO level as a hole-transporting material lies at the carbazole dendron. The HOMO level of the carbazole dendron was estimated from the onset voltage of the oxidation in each dendrimer.[2b,11c] The HOMO levels were **ZnPG1-1** (5.59 eV), **ZnPG1-2** (5.44 eV), and **ZnPG2-2** (5.42 eV). Simultaneously, the HOMO levels of the asymmetric-type dendrimers were estimated. The HOMO levels of the asymmetric-type dendrimers **Cz2−DPAn** ($n$ = 1,2,3) were all 5.41 eV. These results show that the HOMO level and generation of the carbazole dendron has a relation, i.e., when the generation of the carbazole increases, the HOMO level increases. On the other hand, even when the phenylazomethine generation increases, the HOMO level does not change.

The OLED devices[22] were fabricated by spin coating the dendrimers.[8] The structure of the devices was ITO/dendrimers/$Alq_3$/CsF/Al, in which the dendrimer acts as the hole-transporting layer (HTL) and $Alq_3$ as the emitting layer (EML). The luminescence property of the OLED with the double layer-type dendrimers **ZnPG1-2**, and **ZnPG2-2** were roughly the same and much more efficient than **ZnPG1-1**(Figure 6). This can be explained by the energy gap between the ITO and the dendrimers. The working function of the ITO is reported to be 4.5–5.1 eV,[23] and therefore **ZnPG1-1** has a larger hole injection barrier than the other two dendrimers. Additionally, for an OLED device, an amorphous film is needed, and the film forming properties of **ZnPG1-2** and **ZnPG2-2** are better than that of **ZnPG1-1** due to the higher molecular weight.

**Scheme 3. Synthesis of the Double Layer-Type Dendrimers**



**Scheme 4. Synthesis of the Asymmetric-Type Dendrimers**



The luminescence property of the device with **ZnPG2-2** efficiently increased by adding only 0.5 equiv of $SnCl_2$(Figure 7). This simple and unique method to enhance the hole-transporting property derived from the metal complexation to the imine sites has been reported for several phenylazomethine compounds[15] and shows that the new layer-type dendrimer also maintains this property even when the phenylazomethine units are not at the surface of the dendrimer.

Next, the same OLED devices using the asymmetric-type dendrimers were fabricated. The device performance obviously decreased when the generation of the phenylazomethine (DPA) increased (Figure 8). In this case, the HOMO levels are the same and the film forming property indicates the opposite result. This result is in contrast to the double layer-type dendrimers, because in the double layer-type dendrimers, the device performance was maintained even as the generation of the phenylazomethine increased. An explanation of this is due the difference in the molecular architecture. In the carbazole−phenylazomethine

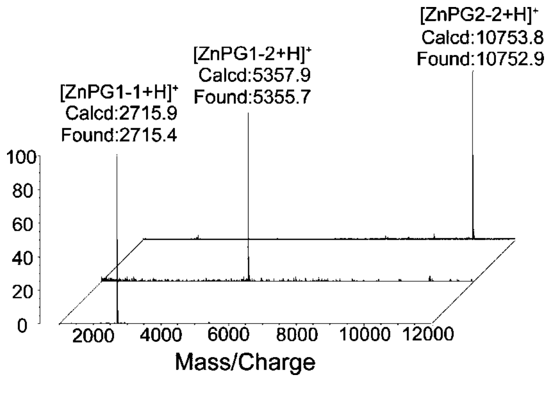


**Figure 1.** MALDI-TOF-MS spectra of double layer-type dendrimers.

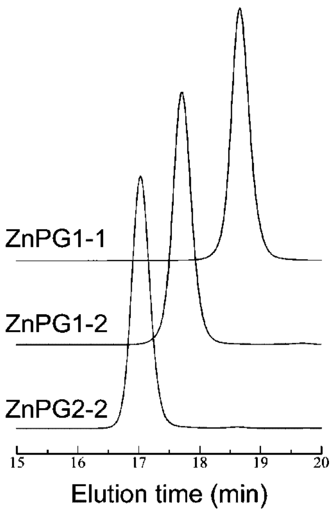


**Figure 2.** Elution curves of SEC measurements of the double layer-type dendrimers by an RI detector. THF was used as the eluent at a flow rate of 1 mL/min.

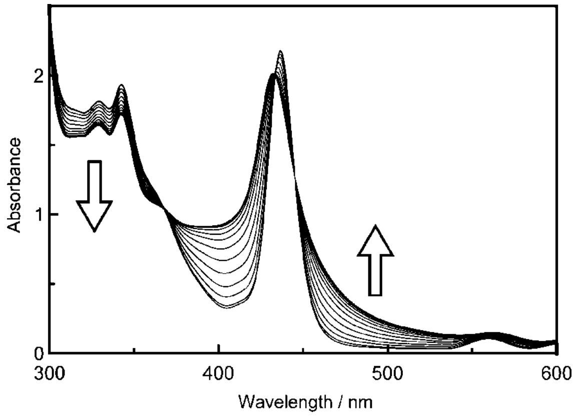


**Figure 3.** UV−vis spectra of the ZnPG2−2 dendrimer during the addition of $SnCl_2$ (solvent is benzene:acetonitrile = 4:1).

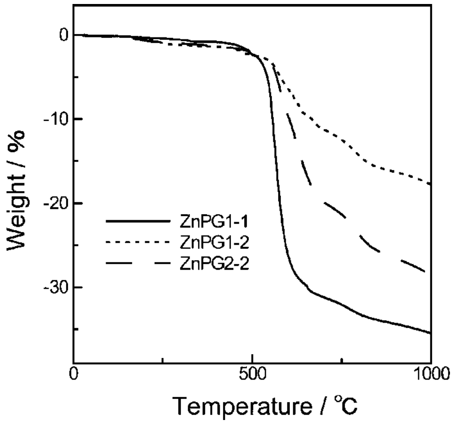


**Figure 4.** Temperature vs weight loss plots of double layer-type dendrimers.

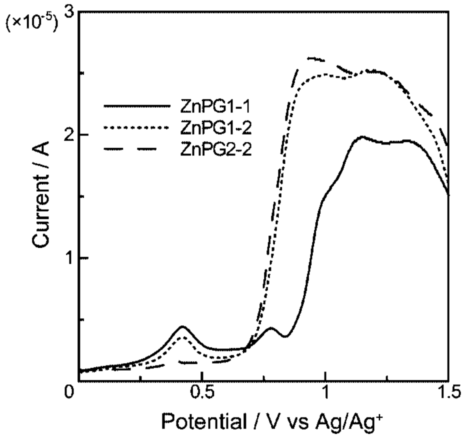


**Figure 5.** The differential pulse voltammograms of double layer-type dendrimers.

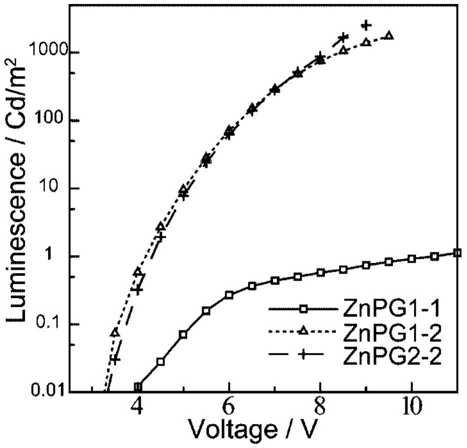


**Figure 6.** Luminance vs voltage characteristics of double-layer OLEDs with CsF/Al cathodes using the double layer-type dendrimers.

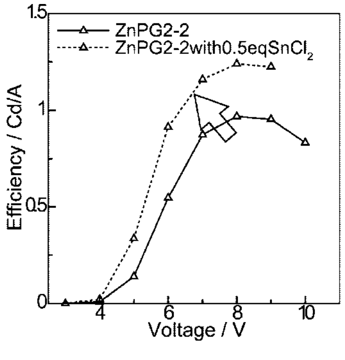


**Figure 7.** Efficiency vs voltage characteristics of double-layer OLEDs with CsF/Al cathodes using **ZnPG2−2** dendrimer with and without $SnCl_2$.

dendrimers, the hole will be mainly transported through the carbazole units due to the higher hole-transporting property and higher HOMO level than the phenylazomethines.[11a,b,15] The outer layer of the double layer-type dendrimer is covered with carbazole units, and therefore the hole can hop through the carbazole units from one side to the other side of the dendrimer and then hop to the next dendrimer. In contrast, in the asymmetric-type dendrimers, the path from one dendrimer to another dendrimer through the carbazole unit is very limited, and it gets worse when the generation of the phenylazomethine increases. Therefore, the hole has to pass through the phenylazomethine units or a circuitous course that will suppress the smooth transport of the hole.

In conclusion, carbazole−phenylazomethine double layer-type dendrimers with the porphyrin core were synthesized and characterized. These dendrimers were thermally stable and could assemble metal ions at the imine sites. By a comparison of the OLED device performance with the asymmetric-type dendrimers, the importance of the molecular architecture was confirmed, and it was proven that the double layer-type dendrimer has an ideal architecture. These results are promising in that this

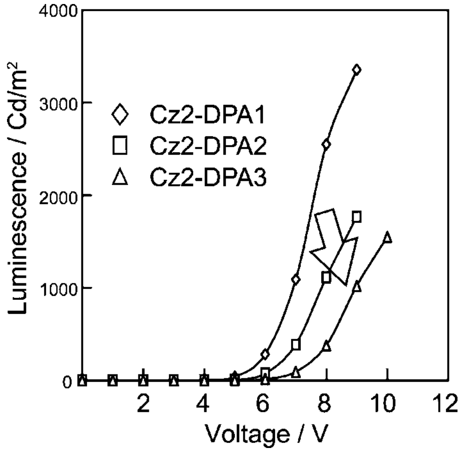


**Figure 8.** Luminance vs voltage characteristics of double-layer OLEDs with CsF/Al cathodes using the asymmetric-type dendrimers.

architecture has potential significance in application of the organic electronics material for several other devices.

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**Supporting Information Available:** The UV−vis titrations, titration curves, and NMR charts. This material is available free of charge via the Internet at http://pubs.acs.org.

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