Synthesis of Asymmetrically Arranged Dendrimers with a Carbazole Dendron and a Phenylazomethine Dendron

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ABSTRACT: Asymmetrically arranged dendrimers with a carbazole dendron and a phenylazomethine dendron were synthesized by the combination of Ullmann reaction and a dehydration reaction in the presence of titanium tetrachloride. Stepwise complexation in the phenylazomethine dendron unit within these dendrimers and SnCl₂ suggests a gradient in the electron density associated with the imine groups. The complexation of the dendrimer changes the HOMO/LUMO energy gap of the dendrimer. We show the dendrimers with higher generations have the larger HOMO values. The most electron-rich molecule, **Cz3-DPA3**, has the highest HOMO value of 5.35 eV and, accordingly, is expected to have the lowest barrier for the hole injection from the ITO electrode (4.6 eV) in OLEDs. However, for the HOMO energy levels of the carbazole dendrimer complex with SnCl₂, the energy levels of the carbazoles did not change based on almost the same redox potentials as those of the dendrimers themselves. Using **Cz3-DPA3** as a hole-transport layer (HTL), only complexation with metal ions results in the enhanced maximum luminescence from 4041 to 10 640 cd/m² by only complexing with SnCl₂ under the nonoptimized conditions. A complexation leads to a high EL efficiency because of the p-type-doped structure of the dendrimers as a hole-transport layer.

Introduction

Branches of the dendrimers^{1,2} with a monodispersed and well-defined structure growing up symmetrically by modular synthesis³ have developed with a regular architecture, producing materials of intriguing properties, such as light harvesting,⁴ catalysis,⁵ and so on, with a better amorphous property and high solubility due to the geometry of these molecules without close packing. We should note that dendrimers, especially rigid ones, can possibly be regularly assembled by packing on a plate without deformation of the molecule⁶ and are expected to expand the field of nanomaterials.^{7,8} The synthetic control to obtain designed dendrimers arranged asymmetrically, such as layered, $^{9-11}$ segmented, 9,12,13 or tailored ones, 14,15 is difficult, requiring stepwise synthetic methodology. Generally, asymmetrically substituted dendrimer building blocks are prepared by interrupting after the first of two possible reactions using a large excess of monomer. Indeed, when preparing asymmetric soft dendrimers with σ bonds, the developing process, which includes many types of reactions with a lower reactivity, is easily applied to asymmetric building blocks. However, asymmetric building blocks with rigid branches consisting of π -conjugated bonds are difficult to prepare because of a few varieties of growth reactions and reacting substituents with high reactivity. Thus, few examples of preparing and developing asymmetrical dendritic copolymers are reported, compared with those of symmetrically substituted ones, and above all, to the best of our knowledge, few examples of rigid asymmetric dendrimers have been reported.16

Organic materials for various electrooptical applications, for example, organic light-emitting diodes (OLE-Ds)¹⁷ and photocells,¹⁸ generally consist of rigid π -conjugated structures with a narrow HOMO–LUMO gap. Above all, a number of dendrimers have been applied in OLEDs^{19–21} designed by their characteristic synthetic procedure, the convergent method. The advantages of adopting monodispersed and well-defined dendrimers as active components in OLEDs are that they can be easily prepared in high purity and have a better amorphous property and high solubility due to their geometry without close packing, resulting in the easier fabrication of thin films by the spin-coating method, a promising approach for large area display applications as well as polymeric materials.

Efforts have been ongoing to develop a novel holetransport polymer for advanced electronic devices. This is a key material for improving the turn-on voltage, luminescence intensity, operation lifetime, full color display capability, durability, reasonable power efficiency, and so on. Generally, such high-performance devices are obtained by developing sequential HOMO/ LUMO energy gradients in the device by introducing the multilayered structure fabricated by repeatedly making thin films. For example, introducing another layer on the ITO electrode, with a HOMO energy level between that of the hole-transporting layer and of the electrode, that is a hole-injecting layer, lowers the energy barrier for hole injection. This approach involves placing the injecting layer between the ITO and the transport layer, such as copper phthalocyanine (CuPc)²² and 4,4',4"-tris(3-methylphenylphenylamino)triphenylamine (*m*-MTDATA),¹⁹ thus resulting in an enhanced EL efficiency. Another approach to develop the characters of the OLEDs has recently been raised by the insertion of thick doped materials such as doped triarylamine, 23,24 poly(vinylcarbazole), 25 polythiophene, $^{26-29}$ and polyaniline, 30,31 resulting in the enhancement of a carrier injection and transport with a lower driving voltage. However, these two approaches require highly layered structures because of their molecular structures and syntheses and the indefinite

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Chart 1. Structures of Dendrimers



functional separation of the buffer and hole transport in one component. Moreover, the use of polymeric materials is restricted by the fabrication of such more complex structures because of the erosion of the fabricated film in advance followed by the method of making thin films, the spin-coating method.

We now report the syntheses of asymmetrically arranged dendrimers with a carbazole dendron (hole transporter) and a phenylazomethine dendron (metal collector) with a definite functional chemical structure. Stepwise complexation in the phenylazomethine dendron unit within these dendrimers and SnCl₂ suggests a gradient in the electron density associated with the imine groups, and the complexation of the dendrimer changes the HOMO/LUMO energy gap of the dendrimer. Only complexation with metal ions results in a high EL efficiency because of the p-type-doped structure of the dendrimers as a hole-transport layer.

Experimental Section

All chemicals were purchased from Aldrich, Tokyo Kasei Co., Ltd., and Kantoh Kagaku Co., Inc. (reagent grade), and used without further purification. UV-vis spectra were obtained using a Shimadzu UV-2400PC spectrometer. ¹H NMR and ¹³C NMR spectra were measured on a JEOL 400 MHz ET-NMR (JMN 400). Cyclic voltammetry experiments were performed with a BAS-100 electrochemistry analyzer. All measurements were carried out at room temperature with a conventional three-electrode configuration consisting of a platinum working electrode, an auxiliary platinum electrode, and a nonaqueous Ag/AgNO₃ reference electrode. The solvent in all experiments was 1,2-dichloroethane, and the supporting electrolyte was 0.1 M tetrabutylammonium hexafluorophosphate. The $E_{1/2}$ values were determined as $1/_2(E_{pa} + E_{pc})$, where E_{pa} and E_{pc} are the anodic and cathodic peak potentials, respectively. All potentials reported are referenced to Fc/Fc+ external and are not corrected for the junction potential.

Conventional OLED devices having the ITO/dendrimer/Alq/ CsF/Al structure were fabricated by spin-coating the dendrimer solutions in chlorobenzene on an ITO-coated glass anode. Alq (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 mm². The current-voltage characteristics were measured using an Advantest R6243 current/voltage unit. Luminance was measured with a Minolta LS-100 luminance meter under 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 $SnCl_2$ (1 equiv vs the dendrimer) in acetonitrile. The yellow solution changed to light orange based on the complexation and evaporated to dryness to give the dendrimer complex.

Cz2 Dendron. To a solution of carbazole (8.35 g, 50.0 mmol) in acetic acid (140 mL) was added potassium iodide (11 g, 66.3 mmol). With stirring, potassium iodate (16 g, 74.8 mmol) was slowly added to the mixture and refluxed for 10 min. The reaction mixture was cooled to room temperature, and then the mixture of iodinated compounds (7.0 g) was obtained by filtration. The mixture was dissolved in acetic anhydride (42 mL) and added boron trifluoride diethyl etherate (0.15 mL) with refluxing for 20 min to yield 9-acetyl-3,6-diiodocarbazole (3.94 g, 39%, two steps) as a residue. A mixture of carbazole (6.38 g, 38.2 mmol), 9-acetyl-3,6-diiodocarbazole (8.0 g, 17.4 mmol), and copper(I) oxide (7.45 g, 52.1 mmol) in N,Ndimethylacetamide (DMAc) (150 mL) was heated in an oil bath at 160 °C for 36 h. The reaction mixture was cooled to room temperature and then filtered through Celite. The filtrate was poured into a large amount of methanol (2 L), and the mixture of acetylated Cz2 dendron was obtained by filtration. The mixture was dissolved in THF (350 mL), DMSO (150 mL), H₂O (10 mL), and then KOH (9.72 g, 0.173 mol) was added, and the mixture was refluxed for 2 h. The reaction mixture was cooled to room temperature, neutralized by HCl, and then poured into water to give the final mixture. Cz2 dendron (4.73 g, 55%, two steps) was isolated by silica gel column chromatography using 4:1 hexane/ethyl acetate with 2% Et₃N from the mixture.¹H NMR (400 MHz, CDCl₃, TMS standard, 20 °C, ppm): δ 8.48 (s, 1H), 8.20 (d, J = 2.0 Hz, 2H), 8.16 (d, J = 8.0Hz, 4H), 7.69 (d, J = 8.8 Hz, 2H), 7.61 (dd, J = 8.4, 2.0 Hz, 2H), 7.42-7.35 (m, 8H), 7.30-7.25 (m, 4H). ¹³C NMR (100 MHz, CDCl₃, TMS standard, 20 °C, ppm): δ 141.68, 139.15, 129.85, 126.14, 125.79, 124.00, 123.03, 120.20, 119.74, 119.58, 111.95, 109.64. MALDI-TOF-MS: 497.2 ([M]+ calcd for C36H23N3: 497.19).

General Procedure for the Ullmann Reaction. A mixture of *p*-iodoacetanilide and the corresponding carbazole dendron and an excess amount of copper(I) oxide in *N*,*N*-dimethylacetamide (DMAc) was heated in an oil bath at 160 °C for 24 h under a N_2 atmosphere. The reaction mixture was cooled to room temperature and then filtered through Celite to remove excess copper complex. The filtrate was evaporated to dryness. The pure product was isolated by silica gel column chromatography.

Cz1-NHAc. The previous procedure was followed using 1.31 g (5.00 mmol) of *p*-iodoacetanilide, 0.930 g (5.56 mmol) of carbazole, and 1.07 g (7.50 mmol) of copper oxide. The product was isolated by silica gel column chromatography using 2:1 hexane/ethyl acetate with $2\% \text{ Et}_3\text{N}$ as eluent, yielding 1.15 g

(77%). ¹H NMR (400 MHz, CDCl₃, TMS standard, 20 °C, ppm): δ 8.14 (d, 7.6 Hz, 2H), 7.74 (d, J = 8.8 Hz, 2H), 7.51 (d, J = 8.8 Hz, 2H), 7.43–7.35 (m, 5H), 7.28 (dd, J = 8.8, 7.6 Hz, 2H), 2.25 (s, 3H). ¹³C NMR (100 MHz, CDCl₃, TMS standard, 20 °C, ppm): δ 168.31, 140.83, 136.92, 133.47, 127.70, 125.85, 123.17, 121.01, 120.21, 119.81, 109.60, 24.72. MALDI-TOF-MS: 299.3 ([M]⁺ calcd for C₂₀H₁₆N₂O: 300.13). Anal. Calcd for C₂₀H₁₆N₂O: C, 79.98; H, 5.37; N, 9.33. Found: C, 79.96; H, 5.52; N, 9.23.

Cz2-NHAc. The above procedure was followed using 0.521 g (2.00 mmol) of *p*-iodoacetanilide, 1.10 g (2.20 mmol) of **Cz2** dendron, and 0.429 g (3.00 mmol) of copper oxide. The product was isolated by silica gel column chromatography using 2:1 hexane/ethyl acetate with 2% Et₃N as eluent, yielding 1.24 g (99%). ¹H NMR (400 MHz, CDCl₃, TMS standard, 20 °C, ppm): δ 8.26 (s, 2H), 8.16 (d, *J* = 7.6 Hz, 4H), 7.83 (d, *J* = 8.8 Hz, 2H), 7.66 (d, *J* = 8.8 Hz, 2H), 7.60 (t, *J* = 8.4 Hz, 4H), 7.41–7.37 (m, 9H), 7.29–7.25 (m, 4H), 2.27 (s, 3H). ¹³C NMR (100 MHz, CDCl₃, TMS standard, 20 °C, ppm): δ 168.39, 141.64, 140.66, 137.63, 132.74, 130.23, 127.82, 126.18, 125.80, 123.77, 123.05, 121.23, 120.21, 119.61, 111.15, 109.63, 24.86. MALDI-TOF-MS: 630.6 ([M]⁺ calcd for C₄₄H₃₀N₄O: 630.24).

General Procedure for the Hydrolysis/Deprotection of the Amide Bond. To a solution of amide in THF and methanol were slowly added water and an excess amount of H₂SO₄. After refluxing for 2 h, the reaction mixture was cooled in an ice bath, neutralized by NaOH(aq), and then extracted with CHCl₃. The organic layer was washed with Na₂CO₃ solution, dried over anhydrous Na₂SO₄, and evaporated to dryness. The pure product was isolated by silica gel column chromatography.

Cz1-NH₂. The previous procedure was followed using 0.303 g (1.01 mmol) of **Cz1-NHAC**, 0.9 mL of water, and 1.0 mL (20 mmol) of H₂SO₄. The product was isolated by silica gel column chromatography using 2:1 hexane/ethyl acetate with 2% Et₃N as eluent, yielding 0.258 g (99%). ¹H NMR (400 MHz, CDCl₃, TMS standard, 20 °C, ppm): δ 8.13 (d, J = 8.0 Hz, 2H), 7.39 (t, J = 7.6 Hz, 2H), 7.33–7.24 (m, 6H), 6.86 (d, J = 6.6 Hz, 2H), 3.85 (s, 2H). ¹³C NMR (100 MHz, CDCl₃, TMS standard, 20 °C, ppm): δ 145.82, 141.38, 128.42, 128.07, 125.63, 122.87, 120.10, 119.33, 115.83, 109.70. MALDI-TOF-MS: 257.2 ([M]⁺ calcd for C₁₈H₁₄N₂: 258.12). Anal. Calcd for C₁₈H₁₄N₂: C, 83.69; H, 5.46; N, 10.84. Found: C, 83.42; H, 5.86; N, 10.33.

Cz2-NH₂. The above procedure was followed using 0.296 g (0.469 mmol) of **Cz2-NHAc**, 0.42 mL of water, and 0.25 mL (4.7 mmol) of H₂SO₄. The product was isolated by silica gel column chromatography using 1:2 hexane/ethyl acetate with 2% Et₃N as eluent, yielding 0.168 g (61%). ¹H NMR (400 MHz, CDCl₃, TMS standard, 20 °C, ppm): δ 8.24 (s, 2H), 8.15 (d, *J* = 8.0 Hz, 4H), 7.56 (t, 9.6 Hz, 4H), 7.43–7.36 (m, 10H), 7.30–7.23 (m, 4H), 6.90 (d, *J* = 8.4 Hz, 2H), 3.89 (s, 2H). ¹³C NMR (100 MHz, CDCl₃, TMS standard, 20 °C, ppm): δ 146.47, 141.71, 141.21, 135.64, 129.77, 128.44, 127.23, 125.99, 125.77, 123.42, 123.01, 120.19, 119.53, 115.95, 111.25, 109.67. MALDI-TOF-MS: 587.3 ([M]⁺ calcd for C₄₂H₂₈N₄: 588.23).

Procedure for the Synthesis of Cz3-NH₂. The aniline derivative substituted by the **Cz3** dendron (**Cz3-NH₂**) was prepared according to the following procedures as well as the reported ones:

Cz1-I₂-NHAc. To a solution of Cz1-NHAc (0.600 g, 2.00 mmol) in acetic acid (25 mL) was added potassium iodide (0.442 g, 2.66 mmol). With stirring, potassium iodate (0.642 g, 3.00 mmol) was slowly added to the mixture and refluxed for 20 min. The reaction mixture was cooled to room temperature, and then the pure product (0.967 g, 88%) was obtained by filtration and washed with NaHCO₃(aq) and water. ¹H NMR (400 MHz, DMSO-d₆, TMS standard, 20 °C, ppm): δ 10.26 (s, 1H), 8.71 (s, 2H), 7.87 (d, J = 8.6 Hz, 2H), 7.71 (d, J = 8.6 Hz, 2H), 7.51 (d, J = 7.8 Hz, 2H), 7.17 (d, J = 7.8 Hz, 2H), 2.12 (s, 3H). ¹³C NMR (100 MHz, DMSO-d₆, TMS standard, 20 °C, ppm): δ 168.41, 139.44, 139.00, 134.67, 130.25, 129.37, 127.03, 123.72, 120.15, 112.09, 83.35, 24.10. MALDI-TOF-MS: 551.0 ([M]⁺ calcd for C₂₀H₁₄I₂N₂O: 551.92). Anal. Calcd for C₂₀H₁₄I₂N₂O: C, 43.51; H, 2.56; N, 5.07. Found: C, 43.57; H, 2.82; N, 4.67.

Cz3-NH₂. The previous procedure of Ullmann reaction was followed using 0.822 g (1.49 mmol) of Cz1-I₂-NHAc, 1.64 g (3.30 mmol) of Cz2 dendron, and 0.644 g (4.50 mmol) of copper oxide. The product was purified by silica gel column chromatography using chloroform as eluent. The above procedure of the hydrolysis/deprotection was followed using 1.4 mL of water and 1.6 mL (30 mmol) of H₂SO₄. The product was isolated by silica gel column chromatography using 2:2:1 hexane/ethyl acetate/chloroform with 2% Et₃N as eluent, yielding 0.685 g (37%, two steps). ¹H NMR (400 MHz, CDCl₃, TMS standard, 20 °C, ppm): δ 8.50-8.27 (m, 8H), 8.16-8.13 (m, 6H), 7.80-7.15 (m, 34H), 7.05-6.78 (m, 4H), 3.97-3.83 (m, 2H). ¹³C NMR (100 MHz, CDCl₃, TMS standard, 20 °C, ppm): δ 146.54, 141.69, 141.50, 140.84, 140.54, 134.84, 134.55, 130.00, 129.29, 129.06, 128.53, 128.33, 128.16, 126.84, 126.46, 126.16, 125.79, 124.80, 123.95, 123.59, 123.02, 120.19, 119.65, 119.57, 116.04, 115.92, 115.80, 112.31, 111.95, 111.37, 111.26, 109.68. MALDI-TOF-MS: 1250.4 ([M]⁺ calcd for C₉₀H₅₆N₈: 1248.46).

General Procedure for the Synthesis of the Asymmetrically Arranged Dendrimers with a Carbazole Dendron and a Phenylazomethine Dendron. To a mixture of Czm-NH₂ (m = 1-3), the corresponding phenylazomethine dendron, DPAn (n = 1-3), and DABCO in chlorobenzene was added TiCl₄ dropwise. The addition funnel was rinsed with chlorobenzene. The reaction mixture was heated in an oil bath at 125 °C for 4 h. The precipitate was removed by filtration. The filtrate was concentrated, and the pure product was isolated by silica gel column chromatography.

Cz1-DPA1. The previous procedure was followed using 0.240 g (0.931 mmol) of **Cz1-NH**₂, 0.254 g (1.40 mmol) of benzophenone (**DPA1**), 0.157 g (1.40 mmol) of DABCO, and 0.132 g (6.98 mmol) of TiCl₄. The product was isolated by silica gel column chromatography using 9:1:1 hexane/ethyl acetate/ chloroform with 2% Et₃N as eluent, yielding 0.245 g (62%). ¹H NMR (400 MHz, CDCl₃, TMS standard, 20 °C, ppm): δ 8.11 (d, 7.2 Hz, 2H), 7.82 (d, J = 7.2 Hz, 2H), 7.53–7.20 (m, 16H), 6.93 (d, J = 8.8 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃, TMS standard, 20 °C, ppm): δ 169.03, 150.59, 140.98, 139.29, 135.97, 132.51, 130.92, 129.52, 129.36, 128.82, 128.22, 127.97, 127.32, 125.71, 123.08, 122.27, 120.14, 119.59, 109.63. MALDI-TOF-Mass: 420.6 ([M]⁺ calcd for C₃₁H₂₂N₂: 422.2). Anal. Calcd for C₃₁H₂₂N₂: C, 88.12; H, 5.25; N, 6.63. Found: C, 87.72; H, 5.48; N, 6.47.

Cz2-DPA2. The previous procedure was followed using 0.0993 g (0.169 mmol) of Cz2-NH2, 0.184 g (0.340 mmol) of DPA2, 0.246 g (2.19 mmol) of DABCO, and 0.104 g (0.547 mmol) of TiCl₄. The product was isolated by silica gel column chromatography using chloroform with 2% Et₃N as eluent, yielding 0.163 g (87%). 1H NMR (400 MHz, CDCl₃, TMS standard, 20 °C, ppm): δ 8.27 (s, 2H), 8.16 (d, J = 7.6 Hz, 4H), 7.77 (d, J = 7.2 Hz, 2H), 7.70 (d, J = 7.2 Hz, 21H), 7.63-6.94 (m, 40H), 6.78 (d, J = 8.4 Hz, 2H), 6.68 (d, J = 8.4 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃, TMS standard, 20 °C, ppm): δ 168.93, 168.68, 168.45, 153.85, 151.99, 151.58, 141.67, 139.20, 138.90, 135.75, 134.23, 131.41, 130.95, 130.49, 130.35, 130.12, 130.04, 129.38, 129.25, 128.82, 128.67, 128.18, 128.02, 127.69, 127.36, 126.07, 125.80, 123.63, 123.04, 122.88, 120.55, 120.34, 120.19, 119.57, 111.30, 109.64. MALDI-TOF-Mass: 1110.4 ([M]⁺ calcd for C₃₁H₂₂N₂: 1109.0). Anal. Calcd for C₈₁H₅₄N₆: C, 87.54; H, 4.90; N, 7.56. Found: C, 87.39; H, 5.06; N, 7.46.

Cz3-DPA3. The previous procedure was followed using 0.425 g (0.340 mmol) of **Cz3-NH**₂, 0.427 g (0.340 mmol) of **DPA3**, 0.246 g (2.19 mmol) of DABCO, and 0.104 g (0.547 mmol) of TiCl₄. The product was isolated by silica gel column chromatography using chloroform with 2% Et₃N as eluent, yielding 0.746 g (88%). ¹H NMR (400 MHz, CDCl₃, TMS standard, 20 °C, ppm): δ 8.51 (s, 2H), 8.30 (s, 4H), 8.15 (d, J = 7.2 Hz, 8H), 7.80–6.95 (m, 88H), 6.89 (t, J = 8.8 Hz, 4H), 6.76–6.55 (m, 12H). ¹³C NMR (100 MHz, CDCl₃, TMS standard, 20 °C, ppm): δ 168.78, 168.54, 168.41, 168.26, 168.12, 154.37, 153.79, 153.71, 153.37, 151.90, 151.78, 151.30, 141.59, 141.39, 139.10, 138.91, 138.67, 135.55, 133.99, 133.82, 133.60, 130.82, 130.48, 130.36, 130.20, 129.98, 129.27, 128.60, 128.06, 127.91, 127.74, 127.50, 126.37, 126.09, 125.70, 125.34, 123.68,





^a Reagents and conditions: (i) KI, KIO₃, AcOH, 20 min; (ii) Ac₂O, BF₃-Et₂O, 10 min; (iii) carbazole, Cu₂O, DMAc, 36 h; (iv) KOH, H_2O , THF, DMSO, 2 h.

123.54, 122.94, 120.83, 120.74, 120.40, 120.10, 119.93, 119.60, 119.49, 111.69, 111.16, 109.55. MALDI-TOF-Mass: 2487.0 ([M]⁺ calcd for $C_{31}H_{22}N_2$: 2486.3).

Results and Discussion

The reactivity and generality of the substrate constructing the phenylazomethine backbone are much higher than those of an arylamine backbone. Although the triarylamine can easily be formed using palladiumcatalyzed reactions, various reaction conditions, such as palladium complex, ligands, and so on, are required, resulting in lower generalities. On the other hand, the formation of the phenylazomethine backbone affords great generality by the dehydration reaction of aromatic amines with aromatic ketones in the presence of titanium(IV) tetrachloride and 1,4-diazabicyclo[2.2.2]octane (DABCO). For these reasons, we considered the strategy to prepare the asymmetrically substituted dendrimers by first introducing a dendritic carbazole unit and then the dendritic phenylazomethines. As shown in Scheme 1, the **Cz2** dendron,³² that is, the carbazole trimer, was obtained by the combination of the iodination,³³ acetylation, and the modified Ullmann condensation³⁴ (Scheme 1). We adopted the acetyl group for the protection of the amines. This is due to the high thermal stability of the amide bond compared with that of the Boc (t-butoxycarbonyl) group that is a traditional protecting group of amines.

The aniline derivatives with a carbazole dendron (**Czm-NH**₂) were obtained from *p*-iodoacetanilide using

the same reactions.³⁵ The convergent approach was employed to synthesize the first-generation (G1) and second-generation (G2) dendrimers. The G1 and G2 substituted aniline derivatives were simply synthesized from *p*-iodoacetanilide, and carbazole or **Cz2** dendron, via the Ullmann condensation to yield **Cz1-NHAc** and **Cz2-NHAc**, respectively (Scheme 2), following the hydrolysis reaction of the amide-protecting unit using sulfuric acid to obtain **Cz1-NH₂** and **Cz2-NH₂**, respectively. Generally, the hydrolysis of the amide can easily proceed in the presence of a strong base such as NaOH, KOH, and so on.³⁵ However, in this case, this hydrolysis reaction cannot proceed when using them.

The synthesis of **Cz3-NH**₂ was carried out with a route like a double-stage convergent method as shown in Scheme 3. This is due to the decreased reactivity of the amine site at the **Cz3** dendron, which can be synthesized by the same procedures as the **Cz2** dendron. We then adopted the growth procedure stacking the **Cz2** dendron on the carbazole unit. First, the iodination of **Cz1-NHAc** was pursued to give **Cz1-I₂-NHAc**, and then **Cz1-I₂-NHAc** was allowed to react with the **Cz2** dendron under the Ullmann reaction conditions successfully yielding **Cz3-NH₂**.³⁶

As shown in Scheme 4, a series of dendrimers substituted asymmetrically (**Czm-DPAn**) were synthesized by the dehydration reaction using TiCl₄ from the corresponding 4-amino-*N*-phenylcarbazoles (**Czm-NH**₂) and phenylazomethine dendron (**DPAn**), which were obtained by a previously reported procedure.^{6,37} These dendrimers were characterized by ¹H and ¹³C NMR spectroscopies, elemental analysis, and matrix-assisted laser desorption/ionization time-of-flight mass spectroscopy (MALDI-TOF-MS).

The addition of SnCl₂ to a chloroform/acetonitrile solution of asymmetrically substituted dendrimers (**Czm-DPAn**) resulted in a complexation with a stepwise spectral change, similar to that for the previously reported dendrimers.^{38–41} During addition of SnCl₂, the solution color of **Cz3-DPA3** changed from light to deeper yellow. We observed that the complexation was complete in 10 min by the spectral change after the addition of SnCl₂; that is, the complexation equilibrium is reached within at least several minutes. Using UV–vis spectroscopy to profile the complexation until an equimolar



Scheme 2. Syntheses of Cz1-NH₂ and Cz2-NH₂^a

^a Reagents and conditions: (i) carbazole, Cu₂O, DMAc, 24 h; (ii) H_2SO_4 , H_2O , THF, MeOH, 2 h; (iii) CzG2 dendron, Cu₂O, DMAc, 24 h.

Scheme 3. Synthesis of Cz3-NH₂^a



Cz3-NH₂

^a Reagents and conditions: (i) KI, KIO₃, AcOH, 20 min; (ii) Cz2 dendron, Cu₂O, DMAc, 24 h; (iii) H₂SO₄, H₂O, THF, MeOH, 2 h.







^a Reagents and conditions: (i) TiCl₄, DABCO, PhCl.



Figure 1. UV–vis spectra changes of **Cz3-DPA3** on stepwise addition of equimolar $SnCl_2$ in $CH_3CN/CHCl_3 = 1/4$. (Inset) Enlargements focusing isosbestic points.

amount of $SnCl_2$ had been added, three changes in the position of the isosbestic points were observed, indicating that the complexation proceeds, not randomly, but stepwise. This result suggests that three different complexes are successively formed upon the $SnCl_2$ addition.

The absorption band around 400 nm attributed to the complex increases with a decrease in the absorption bands around 320 nm, attributed to the phenylazomethine unit. The spectra of **Cz3-DPA3** gradually changed,

Table 1. Physical Data of the Dendrimers (Czm-DPAn)and Their Complex with 1 SnCl2

| | • | |
|----------------------------|--|-------------------|
| | oxidation potential/ V vs Fc/Fc ^{+a} | calcd HOMO/ eV |
| Cz1-DPA1 | 0.687, 0.882 | -5.49 |
| Cz1-DPA1-SnCl ₂ | 0.616, 0.753 | -5.42 |
| Cz2-DPA2 | 0.616, 0.753 | -5.41 |
| Cz2-DPA2-SnCl ₂ | 0.594, 0.739 | -5.39 |
| Cz3-DPA3 | 0.555, 0.735 | -5.35 |
| Cz3-DPA3-SnCl ₂ | 0.538, 0.734 | -5.34 |
| | | |

^a Measured in 1,2-dichloroethane.

with an isosbestic point at 374 nm up to the addition of 1 equiv of SnCl₂ (Figure 1). The isosbestic point then shifted upon the further addition of SnCl₂ and appeared at 372 nm between 1 and 3 equiv, moving to 368 nm when adding between 3 and 7 equiv. Overall, the number of added equivalents of SnCl₂ required to induce a shift was in agreement with the number of imine sites present in the different layers of Cz3-DPA3. The titration results suggest that the complexation proceeds in a stepwise fashion from the core imines to the terminal imines of Cz3-DPA3 (Scheme 5).42 A similar stepwise complexation was also observed with Cz2-**DPA2**. From the theoretical calculations, the stepwise complexation requires the larger equilibrium constants with at least 10 times larger of the inner imine sites than the outer ones.³⁹ In other words, the basicity for

 Table 2. Electroluminescence Properties for the Devices

| HTL | turn-on | max brightness/ | current density ^a / | driving | current density ^{b/} | EL eff ^{b/} | quantum |
|------------------------------|-----------|-------------------|--------------------------------|-------------------------|-------------------------------|----------------------|---------------------|
| | voltage/V | cd/m ² | mA/cm ² | voltage ^b /V | mA/m ² | lm/W | eff ^b /% |
| Cz3-DPA3 | 5.6 | 4041 | 18.4 | 9.2 | 7.86 | 0.43 | 0.42 |
| Cz3-DPA3 + SnCl ₂ | 3.0 | 10640 | 227.3 | 6.1 | 7.04 | 0.73 | 0.46 |

^a Taken at 9 V. ^b Taken at 100 cd/m².





^{*a*} This complexation thermodynamically proceeds in a stepwise fashion from the core imines to the terminal ones, according to the electron gradients of **Cz3-DPA3**.

the inner phenylazomethine is higher with increasing the generation number, and the stability of the phenylazomethine– $SnCl_2$ complex intensified. In another aspect, the higher coordination constant of inner imines conducts phenylazomethine dendron to the highly electron-donating substituent.

The electrochemical properties of the dendrimers were studied by cyclic voltammetry. The HOMO values are determined from the first oxidation potential values with respect to ferrocene (Fc), as shown in Table $1.^{43}$ All the dendrimers displayed quasi-reversible oxidation waves attributed to the oxidation of triarylamine in the region between 0.2 and 1.4 V vs Fc/Fc⁺. We have found that comparing the generation of the asymmetrically arranged dendrimers, the reduced oxidation potential of the Czm unit was observed on the basis of the electron richness and, therefore, the HOMO values with higher generations. Indeed, the most electron-rich molecule, Cz3-DPA3, has the highest HOMO value of -5.35 eV and, accordingly, expected to have the lowest barrier to hole injection from the ITO electrode (-4.6)eV) in OLEDs. Complexing with 1 equiv of SnCl₂, redox waves resulted with almost the same potential (-5.34)eV) as previously observed in the oxidation wave of the carbazole dendron. However, an additional stable redox wave attributed to the reduction of the azomethinemetal complex unit was not observed within the potential range.

A bright green emission was observed for all the cells when a positive dc voltage was applied to the ITO electrode. The electroluminescence spectrum was in accord with the photoluminescence spectrum of Alq. This indicates that the electroluminescence originates from the recombination of holes and electrons injected into Alq. For the two-layer OLEDs, **Cz3-DPA3** and its complex with the SnCl₂ films were then employed as the hole-transporting layer. To a solution of the dendrimer in chloroform was added a solution of SnCl₂ (1 equiv vs the dendrimer) in acetonitrile. The yellow solution changed to light orange based on the complex-



Figure 2. Luminance–voltage characteristics of double-layer OLEDs with CsF–Al cathodes using **Cz3-DPA3** (diamond) and its complex (square) with 1 SnCl_2 as HTL.

ation and evaporated to dryness to give the dendrimer complex. The films were obtained by the spin-coating method. As shown in Figure 2 and Table 2, the low driving voltage and enhanced efficiency were followed by simply assembling the metal ions. The turn-on voltage was reduced from 5.6 to 3.0 V, and the maximum luminescence was enhanced from 4041 to 10640 cd/m² by only complexing with SnCl₂ under the nonoptimized conditions. Also, the current performance of the G3–Sn complex was over 10 times greater (227.3 mA/ cm²) for the same forward driving voltage (9 V) compared to that of the uncomplexed device (18.4 mA/cm²). The threshold voltages for obtaining a luminance of 100 cd/m² were 9.2 and 6.1 V for the cells, respectively.

For the HOMO energy levels of the carbazole– dendrimer complex, the energy levels of the carbazoles did not change on the basis of the same redox potentials when complexing. When considering the influence of doping on the turn-on voltage and the performance at a lower driving voltage, the reduction in the bulk resistance followed by the p-type doping facilitates efficient hole injection into HTL.⁴⁰ The reduction of space charge layers at the interface of the ITO and the dendrimer complex leads to efficient carrier injection due to tunneling.

In summary, we have synthesized asymmetrically arranged dendrimers with a carbazole dendron and a phenylazomethine dendron. Stepwise complexation in the phenylazomethine dendron unit within these dendrimers and $SnCl_2$ suggests a gradient in the electron density associated with the imine groups, and the complexation of the dendrimer changes the HOMO/ LUMO energy gap of the dendrimer. Only complexation with metal ions results in a high EL efficiency because of the p-type-doped structure of the dendrimers as a hole-transport layer as our past research. A development study about the mechanism for the development of hole-transport in OLEDs is now in progress.

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Supporting Information Available: Cyclic voltammograms of Cz1-DPA1, Cz2-DPA2, and Cz3-DPA3 in 1,2dichloroethane. This material is available free of charge via the Internet at http://pubs.acs.org.

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