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## Novel Triarylamine Dendrimers as a Hole-Transport Material with a Controlled Metal-Assembling Function

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Triarylamine dendrimers are unique molecules possessing multiple functions such as redox, fluorescence, and ferromagnet. Especially, triarylamine derivatives as a hole-transport material play an important role in electronic devices such as organic light-emitting diodes (OLEDs) and photo cells.<sup>1</sup> However, these monomeric molecules<sup>2</sup> do not exhibit a high hole-transport efficiency because of their crystallinity, low mold ability, or low thermal stability. Convenient solution processing has been desired as an easy preparation of devices with a large area. To resolve their problems, we should employ the dendritic molecules, whose spherelike rigid structure makes it easy to prepare a homogeneous film by casting. To make the dendritic molecule act as an efficient hole-transport compound, a novel charge-transport system needs to be constructed through the dendron shell between the hole-transport core.<sup>3</sup> Recently, we found a novel stepwise radial complexation in the phenylazomethine dendrimer (DPA), in which the location and number of the metal ion are precisely controllable in the phenylazomethine units.<sup>4</sup> Here, we report the synthesis and the structure of novel phenylazomethine dendrimers with an arylamine as the core. The novel dendrimer is applicable as a hole-transport material in an EL device, using metal-assembling properties in which the metal acts as a mediator of the hole transfer.

The phenylazomethine dendrimer is synthesized up to the fourth generation by a convergent method via dehydration of aromatic ketones with aromatic amines.<sup>4b,5</sup> Therefore, the amino group was first introduced into the terminal portion of TPA. The Pd coupling reaction of bromonitrobenzene with TPA was carried out through a combination of lithiations and Zn transmetalations.<sup>6</sup> The resulting nitro-substituted TPA was reduced with NaBH<sub>2</sub>S<sub>3</sub> that is prepared by mixing NaBH<sub>4</sub> with S, to obtain TPA-NH<sub>2</sub>.<sup>7</sup> TPA-DPA G1, G2, G3, and G4 are synthesized by the dehydration of TPA-NH<sub>2</sub> with the G1, G2, G3, and G4 dendrons, respectively, in the presence of titanium(IV) tetrachloride and 1,4-diazabicyclo[2.2.2]octane (DABCO) (Chart 1, Table 1). These dendrimers were obtained in over 60 wt % yield (see Supporting Information, S1–3).

Size exclusion chromatography (SEC) measurements with a differential viscometer and laser light scattering and RI detector (triple detector SEC: Viscotek Corp.) revealed that the molecular size of TPA-DPA G4 was larger than that of DPA G4 in THF solution. The radii of TPA-DPA G4 and DPA G4 were determined to be 2.11 and 1.64 nm, respectively.<sup>8</sup> The Mark–Houwink plots (Mark–Houwink–Sakurada equation:  $[\eta] = KM^a$ )<sup>9</sup> became a plateau over larger generations (G4 and G3, see S4). The slopes are close to zero, which means that these dendrimers have a rigid sphere structure like a globular protein. Therefore, TPA-DPA is suggested to have a spherelike shape in comparison with DPA, because the dendrimer of TPA has the trifunctional core.

The results of the structural analysis by SEC are electrochemically supported.<sup>4b,10</sup> The shell-effect was observed by the cyclic voltammograms of the dendrimers. The TPA unit of the core shows

Chart 1. Structure of TPA–DPA Dendrimers

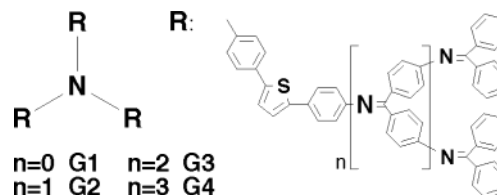


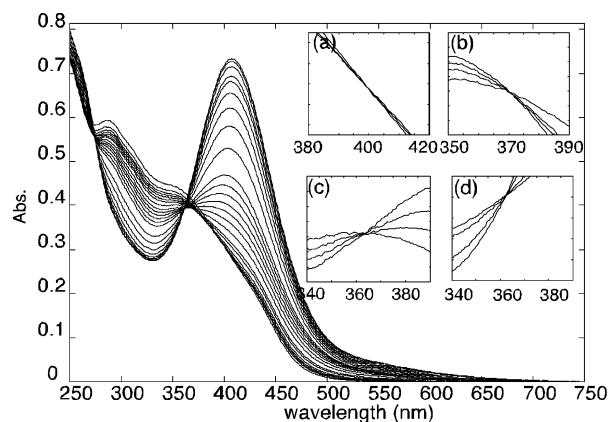
Table 1. Molecular Weights and Related Values of TPA–DPA

TPA–DPA	$M_{\text{calc}}$	yield (%)	MALDI-TOF-mass	$M_n$	$R_h$ (nm)
G1	1257.63	94	1256.7	1560	0.96
G2	2332.94	74	2332.4	2280	1.35
G3	4483.54	69	4483.1	4210	1.69
G4	8784.76	67	8782.7	8050	2.11

a redox wave of the N/N<sup>•+</sup> couple at 0.5 V versus Ag/Ag<sup>+</sup> in the cyclic voltammetry. The redox wave became broadened with an increase in the generation (S5). The broad waves are caused not by the decrease in the diffusion coefficient but by the electron-transfer rate, because the diffusion coefficients calculated using the hydrodynamic radius have the same order of G1 and G4 that were determined to be  $4.92 \times 10^6$  and  $2.24 \times 10^6$  cm<sup>2</sup> s<sup>-1</sup>, respectively. An increase in the distance between the electrode and the core with an increase of the generation results in a decrease in the electron-transfer rate. This suggests that the shell-effect of the dendrimer is occurring. TPA–DPA G4 associated with 1 equiv of SnCl<sub>2</sub> on the electrode shows a reversible redox wave at 0.5 V, which suggests that SnCl<sub>2</sub> promotes the mediation of the electron transfer in the dendrimer (S6).

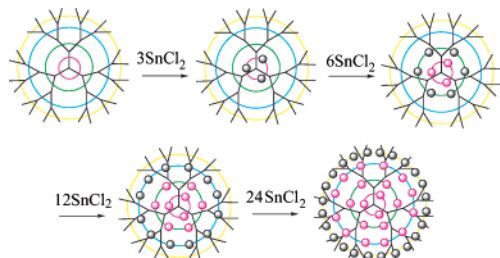
The metal-assembling property of the TPA–DPAs is confirmed by a spectroscopic measurement. During the addition of SnCl<sub>2</sub>, we found a complexation behavior of TPA–DPA G4 similar to that of DPA. Using UV–vis spectroscopy to monitor the titration until an equimolar amount of SnCl<sub>2</sub> had been added, we observed four changes in the position of the isosbestic point, indicating that the complexation proceeds not randomly but stepwise. An isosbestic point appears when a compound is quantitatively transformed into another by complexation, so the four different isosbestic points we observed suggest that four different complexes are successively formed upon SnCl<sub>2</sub> addition.

The absorption band around 400 nm attributed to the complexation increases with a decrease in the absorption bands around 320 nm that are attributed to the phenylazomethine unit. The spectra of TPA–DPA G4 gradually changed, with an isosbestic point at 395 nm due to the addition of 3 equiv of SnCl<sub>2</sub> (Figure 1a). The isosbestic point then shifted upon the further addition of SnCl<sub>2</sub> and appeared at 370 nm between 4 and 9 equiv of SnCl<sub>2</sub> (Figure 1b). Between the addition of 10 and 21 equiv of SnCl<sub>2</sub>, an isosbestic



**Figure 1.** UV-vis spectra of TPA-DPA G4 complexed with  $\text{SnCl}_2$ . (a) The spectral change during the addition of 0–3 equiv of  $\text{SnCl}_2$  (isosbestic point at 395 nm). (b) The spectral change during the addition of 4–9 equiv of  $\text{SnCl}_2$  (isosbestic point at 370 nm). (c) The spectral change during the addition of 10–21 equiv of  $\text{SnCl}_2$  (isosbestic point at 363 nm). (d) The spectral change during the addition of 22–45 equiv of  $\text{SnCl}_2$  (isosbestic point at 361 nm).

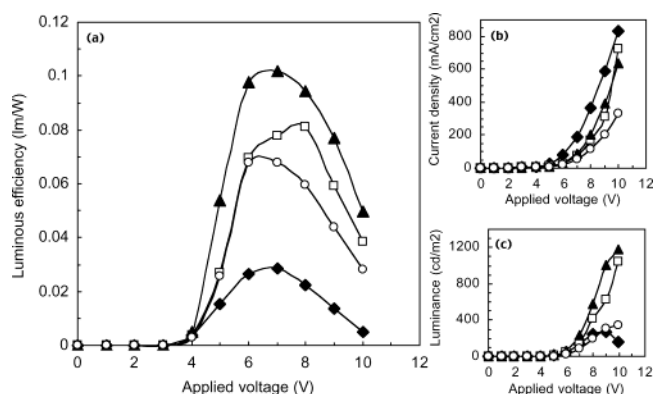
**Scheme 1.** Schematic Representation of Stepwise Complexation of TPA-DPA G4 with  $\text{SnCl}_2$



point appeared at 363 nm (Figure 1c), moving to 361 nm when between 22 and 45 equiv of  $\text{SnCl}_2$  was added (Figure 1d). Overall, the number of added equivalents of  $\text{SnCl}_2$  required to induce a shift was in agreement with the number of imine sites present in the different layers of TPA-DPA G4. The titration results suggest that the complexation proceeds in a stepwise fashion from the core imines to the terminal imines of TPA-DPA G4 as shown in Scheme 1.

A similar stepwise complexation was also observed with TPA-DPA G3 and TPA-DPA G2 (S7). These results further supported the idea that metal ions are incorporated in a stepwise fashion, first filling the layers close to the dendrimer core and then progressively filling the more peripheral layers.<sup>11</sup>

Organic light-emitting diodes (OLEDs) were fabricated, which used the TPA-DPA G1–G4 and the TPA-DPA-metal complexes (G1–G4) as the hole-transport materials and Alq as a luminance layer (S11). The precisely controlled TPA-DPAs with one  $\text{SnCl}_2$  versus the azomethine bonds act as an excellent hole-transport material, even though TPA-DPAs without metal ions do not show EL activity (S12). The EL performances of the devices using the TPA-DPA-metal complexes are drastically increased (ca. 20 times) by metal complexation (Figure 2). The current versus the applied bias voltage is lower, and the efficiency becomes higher by the complexation. Only one  $\text{SnCl}_2$  plays an important role as a hole carrier through the dendron shell and enhances the hole-transport ability of TPA-DPA.<sup>12</sup> The increasing efficiency of OLED in the generation is based on the processibility of dendrimer.



**Figure 2.** Performance of OLED used TPA-DPA as the hole-transport layer. That of TPA-DPA G1 is the  $\blacklozenge$  line. That of TPA-DPA G2 is the  $\square$  line. That of TPA-DPA G3 is the  $\blacktriangle$  line. That of TPA-DPA G4 is the  $\circ$  line. (a) Efficiency of OLED. (b) Turn-on voltage of OLED. (c) Maximum luminance of OLED.

As compared to the generation, TPA-DPA G3 shows the best luminance intensity in its dendrimers.

In conclusion, we demonstrated the enhancement of the hole-transport ability using only one assembled metal in the dendrimer.

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**Supporting Information Available:** Synthetic procedures and additional data (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (12) The addition of equimolar amounts of  $\text{SnCl}_2$  increases the conductivity of the TPA-DPA G3 film to  $1.6 \times 10^{-8}$  S/cm, which results in an increased efficiency of OLED.

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