

Novel Dendrimers Having a Fine-controlled Metal Complexation as a Unique Hole-transport Material

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Organic materials for various electro-optical applications, for example, organic light-emitting diodes (OLEDs) and photocells generally consist of rigid π -conjugated structures with a narrow HOMO-LUMO gap. Above all, a number of dendrimers have been applied in OLEDs designed by their characteristic synthetic procedure. 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.

Asymmetrically arranged dendrimers (**Czm-DPA_n**, Fig. 1) with a carbazole dendron and a phenylazomethine dendron were precisely synthesized by the combination of Ullmann reaction and a dehydration reaction in the presence of titanium tetrachloride. The addition of SnCl₂ to a chloroform/acetonitrile solution of dendritic asymmetrically substituted dendrimers (**Czm-DPA_n**) resulted in a complexation with a stepwise spectral change, similar to that for the previously reported dendrimers. The spectra of **Cz3-DPA3** gradually changed, with an isosbestic point at 374 nm up to the addition of 1 equiv of SnCl₂ (Fig. 2). 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**.

Compared with generations of the dendrimers for the simple device structure (ITO/**Czm-DPA_n**/Alq/CsF/Al), the device characteristics were strongly dependent on their generation number. For example, the performance was enhanced in higher generation of the carbazole dendron and reduced of the phenylazomethine dendron. For the two-layer OLEDs, we then employed the dendrimer complexes with SnCl₂ as a hole-transporting layer. The low driving voltage and enhanced efficiency were followed by simply assembling of the metal ions in the dendrimer (Fig. 3).

We discussed the energy levels of the dendrimer and its complex by cyclic voltammetry. For **Cz3-DPA3**, complexing with 1 equivalent of SnCl₂, redox waves resulted with almost the same potential (-5.3 eV) as observed in the dendrimer itself. Thus, we consider the role of complexation with metal ions as the change in the electronic structure within the dendrimer film by the complexation.

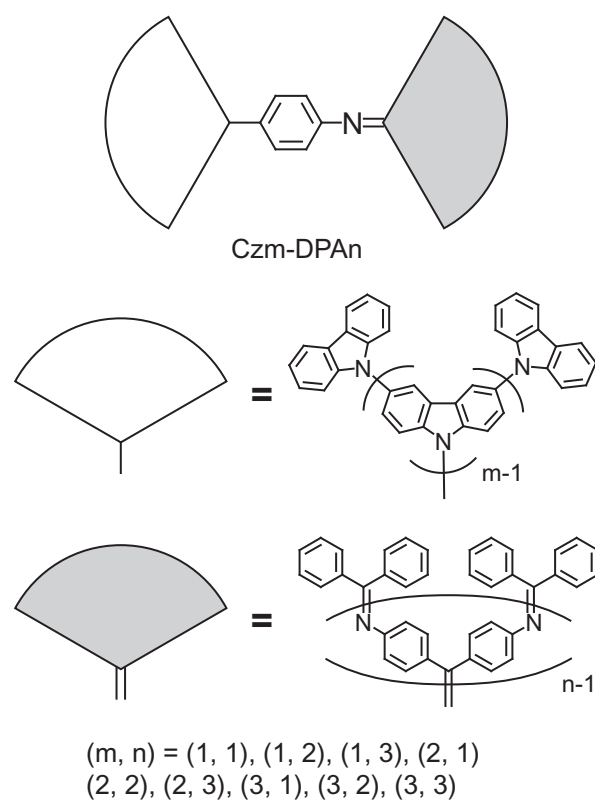


Figure 1. Structures of the dendrimers

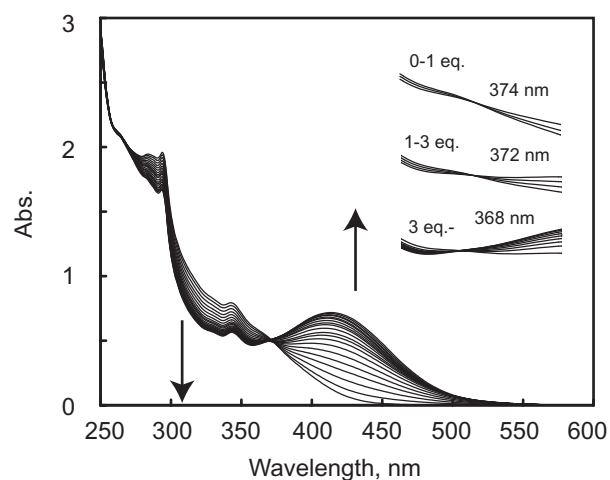


Figure 2. UV-vis spectra changes of Cz3-DPA3 on stepwise addition of equimolar SnCl₂. (Insert) Enlargements focusing isosbestic points.

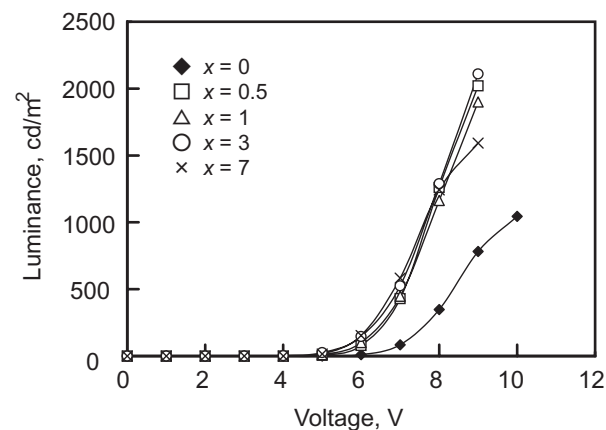


Figure 3. Luminance-voltage characteristics of double-layer OLEDs using Cz3-DPA3 and its complex with x equiv. of SnCl₂ as HTL.