

## Synthesis and Luminescent Properties of Light Harvesting Dendrimers Encapsulated Fluorescent Dyes

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### Abstract

New blue light emitting branched molecules were synthesized by reacting 3,5-bis-(3,5-bis-benzyloxy)-benzoic moiety or 3,5-bis-(3,5-bis-benzyloxy-benzyloxy)-benzoic moiety with biscarbazoyl vinyl biphenyl moiety by dicyclohexylcarbodiimide (DCC) catalyzed esterification. Similar synthetic strategy was also applied to prepare a red light emitting dendrimer. In this paper, we described two blue emitting dendrimers for investigating the effect of the dendronized structures on photoluminescence (PL) and electroluminescence (EL). EL properties of the dendrimers were investigated using heterostructured samples in detail.

### 1. Introduction

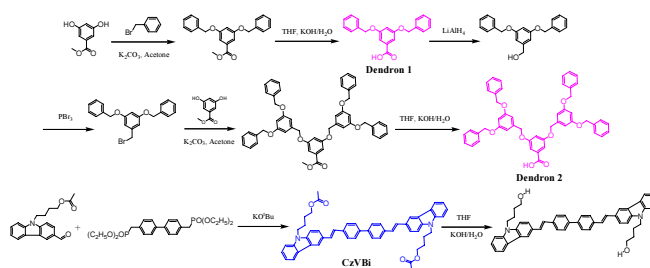
Recently, semiconducting organic materials have attracted much interest as good candidates in electronics and optoelectronics.<sup>1-5</sup> Among their many application fields, electroluminescence (EL) devices using small molar mass organic materials becomes a most highlighted technology that is ready to apply them to the practical applications such as flat-panel or flexible display devices.

In order to improve the EL efficiency, peripheral-to-core energy transfer system based on light harvesting  $\pi$ -conjugated dendrimers were often synthesized. In the solid state, fluorophores in the polymer (more generally, in the host-guest systems), are too labile to induce an intermolecular interaction and aggregation, which results in excimer formation and reduction of the overall emission efficiency. Here we demonstrate that the blue emitting dendrimers display EL characteristics affected by the sterically controlled geometry.

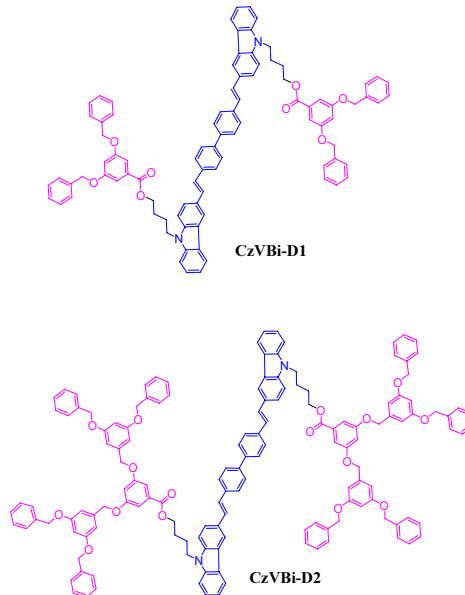
### 2. Results

We only show the EL properties of blue emitting dendrimer in this paper. The synthetic procedures and

structures of the dendrimers are demonstrated in Scheme 1 and 2.



**Scheme 1.** Synthetic procedures for the dendrons and core carbazolyl unit.



**Scheme 2.** Synthetic procedures for the dendrons and core carbazolyl unit.

First, benzyl ether type dendron was synthesized and the carboxylic acid functional group was used for

anchoring into the carbazoyl core unit. DCC catalyzed esterification was conducted to make two blue light emitting dendrimers. (Dendrimer 1 & 2). In this study, dendrimer 1 and 2 were denoted to be CzVBi-D1 and CzVBi-D2, respectively.

The newly synthesized dendrimers are well soluble at room temperature in common organic solvents such as chloroform, THF, acetone, and chlorobenzene and display good self-film forming properties.

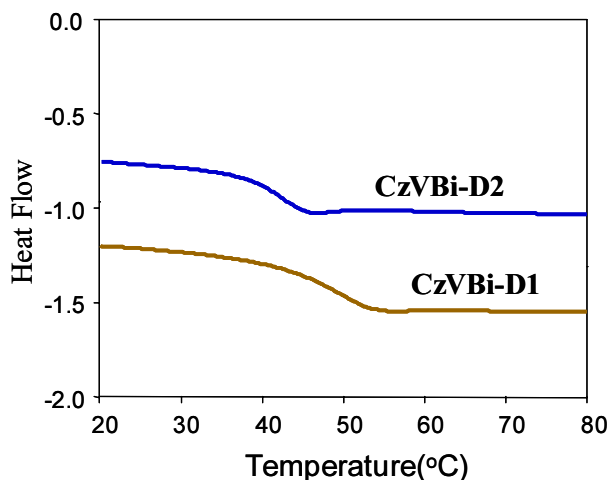


Figure 1. DSC thermograms of two dendrimers.

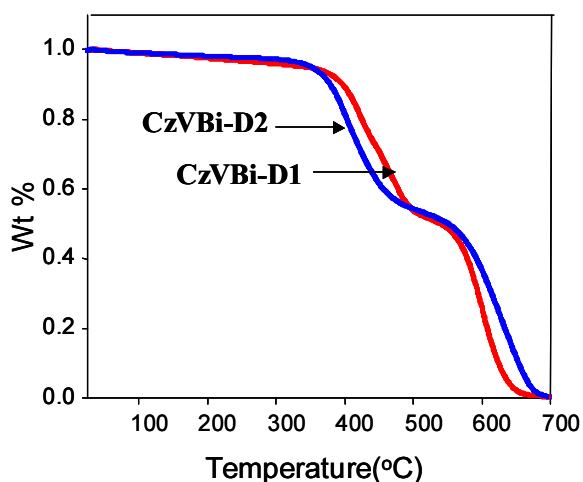


Figure 2. TGA thermograms of two dendrimers.

The glass transition temperatures ( $T_g$ s) of the dendrimers obtained by DSC are 43 °C for CzVBi-D1 and 38 °C for CzVBi-D2. No discernable melting behaviors were observed in the DSC thermograms of these dendrimers. (see Figure 1) Thermal decomposition temperatures are similar but CzVBi-

D1 exhibited a better stability slightly due to smaller concentration of the benzyl ether moiety.

Electrochemical analysis was performed to determine the redox ionization potentials of the synthesized compounds. The oxidation and reduction potentials are closely related to the HOMO and LUMO levels of the analyzed compounds and thus can provide important information regarding the energy transfer process. Cyclic voltammograms were recorded in the film sample and potentials are given relative to an internal ferrocene reference ( $Fc/Fc^+$ ). The dendrimers in acetonitrile have one reversible oxidation ( $E_{ox}^{onset}$ ). Unfortunately, the reduction potentials were irreversible, so we cannot estimate their HOMO and LUMO energies accurately. In order to determine the LUMO levels, we combined the oxidation potential in CV with the optical energy bandgap ( $E_g^{opt}$ ) resulting from the absorption edge of the electronic spectrum.

The HOMO levels of CzVBi, CzVBi-D1, and CzVBi-D2, are determined to be 5.33, 5.23, and 5.25 eV, respectively. (Table 1) Using the lowest bandgap energy in the absorption spectrum, we determined the LUMO levels of the dendrimers. Using these information we can draw the energy diagram that can be expected for EL devices. (Figure 3).

Table 1. Energy levels of the core dye, two dendrimers.

	Electrochemical Analysis	Spectrum Analysis		
	$E_{HOMO}$ (eV)	$E_{LUMO}$ (eV)	$\Delta E_g$	$\lambda_{cut-off}$ (nm)
CzVBi	5.33	2.56	2.77	449nm
CzVBi-D1	5.23	2.49	2.74	452nm
CzVBi-D2	5.25	2.48	2.77	448nm

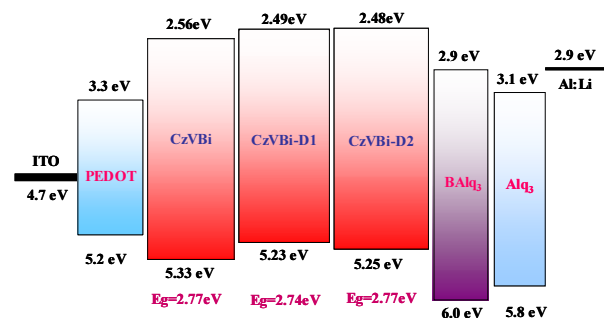


Figure 3. Band diagram of the EL devices.

In Figure 4, the absorption and PL spectra were overlaid to display the feature of the emission. All

three samples showed similar characteristics in solutions.

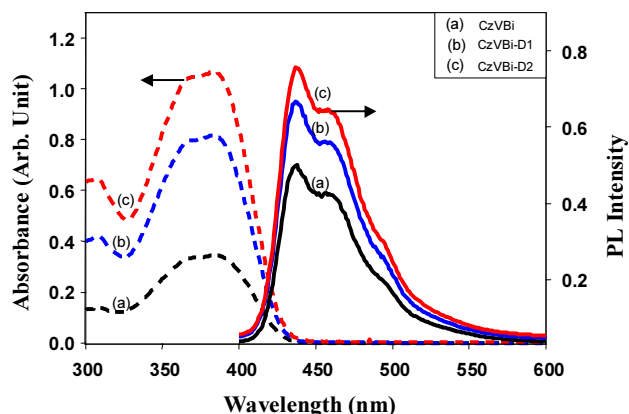


Figure 4. Absorption and PL spectra of the core dye, CzVBi-D1, and CzVBi-D2 in chloroform.

Time-resolved PL spectroscopy has been employed to obtain further information on the emission dynamics of the present dendrimers. Figure 5 displays the optic setup for monitoring the PL decay. For time-resolved PL analysis, all samples were excited by 360-400 nm pulses generated by frequency-doubling of the 800 nm 100 fs pulse from a mode-locked Ti: sapphire laser oscillator (Coherent, Chameleon). The PL kinetic profiles were recorded using a time-correlated single photon counting (TCSPC, EG&G Ortec) setup equipped with a photon-counting MCP-PMT (Hamamatsu) detector. (Figure 5) Figure 6 presents the PL decay profiles of CzVBi, CzVBi-D1, and CzVBi-D2. It displays the PL decay profiles of the dendrimer films

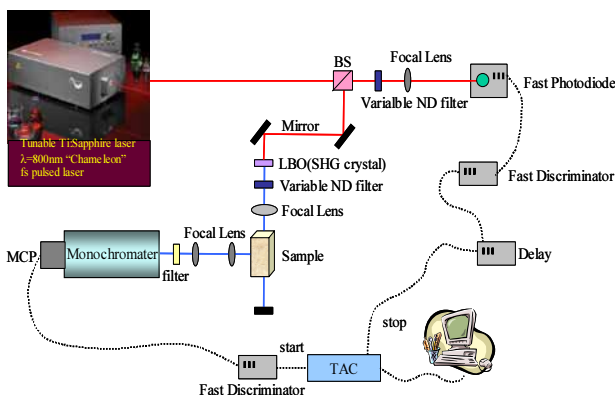


Figure 5. Optic setup for time correlated single photon (TCSPC) counting experiment.

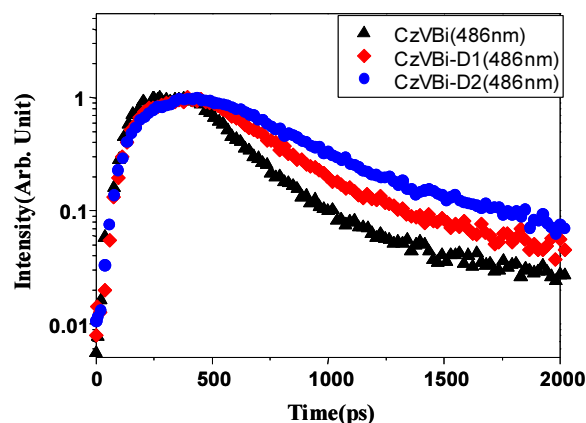


Figure 6. Time-resolved PL signal profiles of two dendrimers in film states. Excitation at 400 nm and PL decay monitored at 486nm.

monitored at 486 nm where fluorescence is originated from the core moiety. The observed decay profiles were well fitted to the single or double exponential decay functions. As is expected, the larger dendrimer, CzVBi-D2 exhibited slower decaying behavior of PL, which is attributed to a higher density of the dendron around the core emitting unit.

We used two dendrimers in light emitting diodes (LEDs) as emissive materials in multi-layered devices. Poly(ethylenedioxy thiophene):poly(styrene sulfonic acid) (PEDOT:PSS) thin film was deposited on indium tin oxide (ITO) as an anode for facilitating hole injection and the dendrimer was coated on it as an emissive layer. A thin 10 nm thick film of BALq was subsequently vapor deposited on the dendrimer as a hole blocking material to confine exciton recombination and limit the loss of the faster moving holes to the cathode. This was followed by deposition of a 10 nm electron injection layer of tris(8-hydroxyquinoline) aluminium ( $\text{Alq}_3$ ) and a LiF/Al electrode sequentially. We found that the EL device with BALq/ $\text{Alq}_3$  layers were much more efficient than those without these layers.

Figure 7 shows the EL emission spectra of devices made of CzVBi-D1 and CzVBi-D2. When we compare two spectra two emission peaks were observed at about 454 and 483 nm. In CzVBi-D1, the intensity at 454 nm is relatively larger than that at 483 nm. The PL origin can be assigned at 480-483 nm in CzVBi core unit. In a larger dendrimer, the intensity at 483 nm was enhanced due to the steric effect. The

higher density of dendron affects the reduction of the interaction between the core dye units. The peak at 454 is conjectured to be an interactive mode.

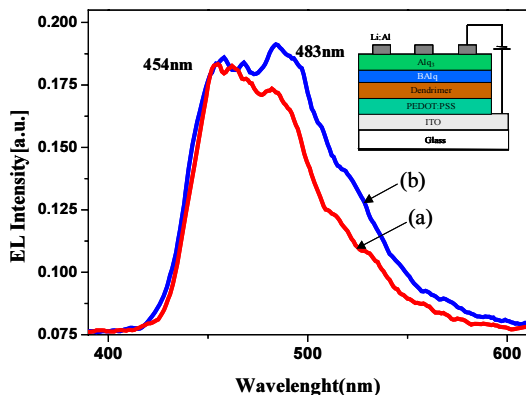


Figure 7. Electroluminescence spectra of multi-layered devices. (a): CzVBi-D1, (b): CzVBi-D2.

The current-voltage and luminance-voltage curves of two dendrimers are shown in Figure 8. The turn-on electric field of two LEDs was around 0.73-0.94 MV/cm. Low value of turn-on field of the device with the HOMO level of the corresponding dendrimer leads to the conclusion that the difference between the work function of the ITO anode and the HOMO level of two dendrimers is relatively small. This, in turn, implies that easier hole injection from the anode controls the turn-on electric field of the present devices, which should become true only when the major carrier is the positive hole.

Using the EL device without BAq layer, we could measure quite low external quantum efficiency around 0.0035-0.0040% of two dendrimers. The poor performance of the dendrimers as emissive EL materials arises from imbalanced charge transport through the dendrimer. In order to increase the efficiency of exciton confinement in an emissive layer, we fabricated multi-layered diodes using two dendrimers as an emissive layer. The second device configuration employed was ITO/PEDOT:PSS (30 nm)/dendrimer (70 nm)/BAq (10 nm)/Alq<sub>3</sub> (10 nm)/Li:Al (100 nm). The luminance and external quantum efficiency were all improved compared to the device without BAq. EL quantum efficiency (0.024-0.029%) was enhanced by efficient exciton confinement and balanced charge transport through the dendrimer.

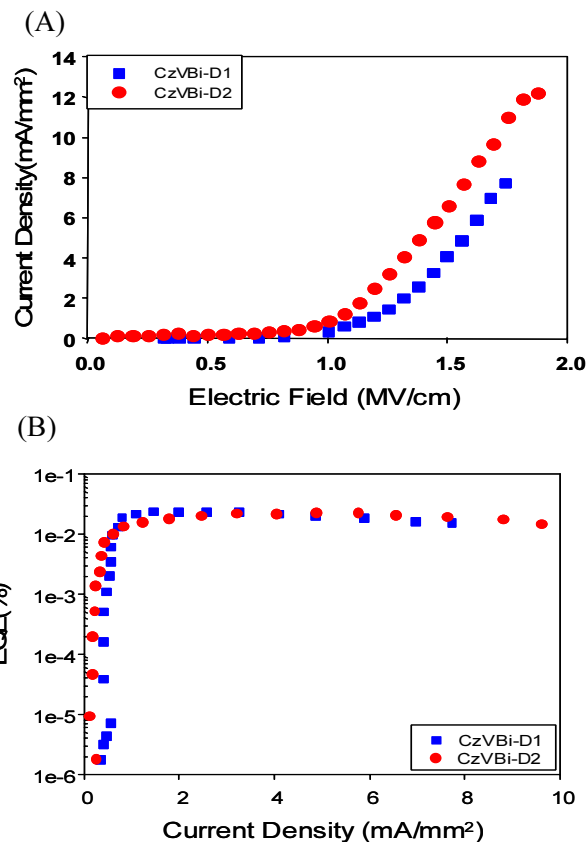


Figure 8. (A) Electric field dependence of current density (B) External quantum efficiency of multi-layered EL device. \*Sample: CzVBi-D1 and CzVBi-D2.

#### 4. Acknowledgements

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