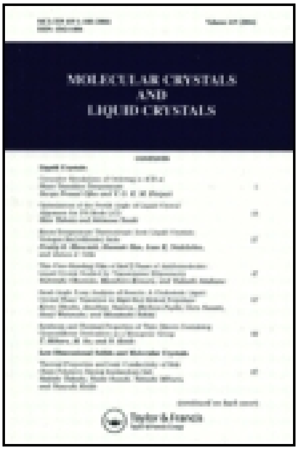

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Photoluminescence and Electroluminescence Characteristics of Benzoxazole Dendrimers

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Various studies have been done using dendrimers as emissive materials for OLEDs, although efficiencies are still significantly lower than those offered by evaporated devices. In this study, dendrimers were synthesized. Photoluminescence (PL) and Electroluminescence (EL) characteristics of Benzoxazole dendrimers were investigated by fabricating the device of structure such as ITO/PVK: Benzoxazole dendrimers: PBD/Li:Al. We used PVK as hole transport material and blended with PBD as electron transport material. The Benzoxazole dendrimers studied here used emissive material. The PL spectra of 1st generation and 2nd generation Benzoxazole dendrimers show blue emission at 438 nm. The EL spectra of 1st generation and 2nd generation Benzoxazole dendrimers were observed at the wavelength of 441 nm and 447 nm.

Keywords: benzoxazole dendrimers; electroluminescenc; photoluminescence

I. INTRODUCTION

Dendrimers have received currently much attention, because of their increasing usability in the materials for the application by accurately controlled functionalities [1–3]. The finding of the synthetic methods and application are very important issue for a material chemist [4]. Several research groups have synthesized and characterized dendritic

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macromolecules with interesting functionalities for various purposes [5–8]. So far, carbosilane as well as Carbosiloxane dendrimers have appeared as one of the important families of dendritic macromolecules [9]. Synthetic methods of silicon-containing dendrimers were reported by a great number of researchers who used the repetitive procedures, such as hydrosilation, alkenylation, alkynylation as well as alcoholysis [10].

Recently, Dendrimer have been studied on organic light emitting devices (OLEDs) as emitting materials. Dendrimers have so far dominated soluble-processed OLEDs, and devices with good efficiencies have been reported. Various studies have been done using dendrimers as emissive materials for OLEDs, although efficiencies are still significantly lower than those offered by evaporated devices. Light emitting dendrimers generally consist of a light-emitting core to which one or more branched dendrons are attached. Surface groups are attached to the distal end of the dendrons to provide the solubility necessary for solution processing. The generation number of a dendrimer is defined as the number of branching levels from the core and this can be used to control intermolecular interactions of the cores on a nanometer scale [11]. In this paper, we report an investigation of a new family of light emitting dendrimers for OLEDs based on the Carbosilane dendrimers including Benzoxazole derivatives and the effect of generation number on both the optical and electroluminescence properties of the materials.

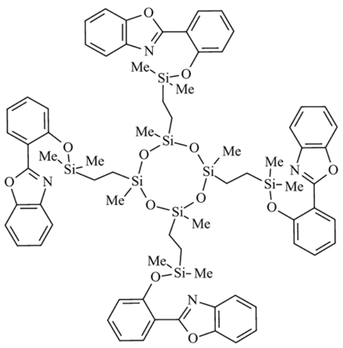
II. EXPERIMENTS

The synthesis of Carbosilane dendrimers including Benzoxazole derivatives on the periphery was established with siloxane tetramer as core, and allyl groups as inner branches was constructed. The parent generations with dichloromethylsilyl groups were prepared by the catalytic hydrosilation of the allylic branches with dichloromethylsilane and the dendrimers with allyl groups was prepared by the addition of allylalcohol [12]. Gn-mBO ($n = 1$, 2, 3, and $m = 4$, 8, and 16) type dendrimers were prepared by the reaction between chlorinated dendrimers and 2-(2-hydroxypheny)Benzoxazole. The purified dendrimers were obtained by chromatographic treatment with silica gel and non-polar solvents. The excess of Benzoxazole moiety and the rest of TMEDA as well as TMEDA-HCl salt were removed by this method. The information about the pure dendrimer was obtained from NMR, GPC, and elemental analysis. The ^{1}H and ^{13}C NMR spectrum of Gn-mBO type dendrimers showed unique spectral properties. The GPC chromatogram viewed single narrow signal from the first to the third generation. Those dendrimers produced a light yellow solid which remained up to 70 ~ 80% yields and exhibited a ready soluble in a wide range of solvents including toluene, THF, chloroform, and so on.

All preparative reactions were performed under dried N_2 atmosphere. The NMR spectra were recorded on a Bruker AC-200 Spectrometer. GPC was performed in THF at 25°C with Waters 515 HPLC pump together with Waters 2410 Refractive Index detector. For GPC, three 7.8×30 cm columns (Ultrastyragel, 7.8×30 cm; 10^3, 10^4, 10^5) were connected in series and calibrated with the narrow molecular weight polystyrene standard.

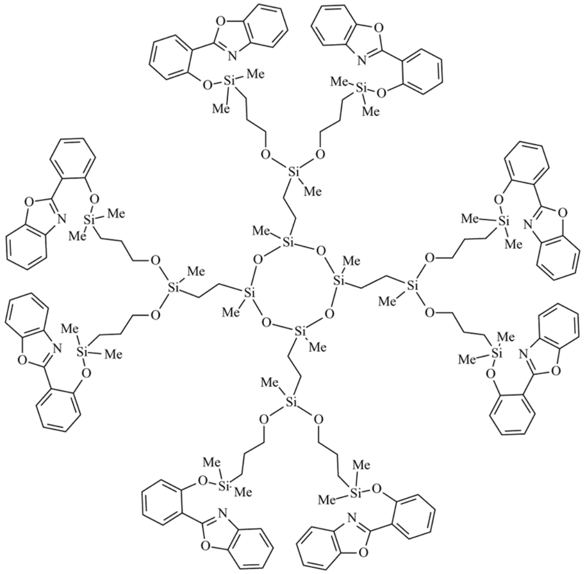
The OLEDs were fabricated on indium-tin-oxide (ITO) coated glass substrates with a sheet resistance of $10\,\Omega/\square$, and the thickness of the ITO was 120 nm. The ITO glass was cleaned using trichloro-ethylene, acetone, iso-propyl alcohol and ultra pure water sequentially for 10 minutes using an ultrasonic cleaner. Prior to film deposition, ITO substrate performed surface treatment by UV-ozone for 1 minute. UV-ozone treatment enhanced the performance of OLEDs. The chemical structures of dendrimers prepared in this study were shown in Figure 1. Poly(9-vinylcarbazole) (PVK) used hole transport material and 2-(4-biphenyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole (PBD) was expected to transport the electrons in the blend layer [13–15]. The PVK: Benzoxazole dendrimers:PBD blend solutions were prepared from chloroform solution of PVK:PBD (1.0%:0.2%) blend by weight dispersed with dendrimer (0.03%).

The ionization potential and the electron affinity of Benzoxazole dendrimers were measured by cyclic-voltammetry carried out with potentionstat 263 A (Seiko EG&G Instrument). We obtained the IP from ITO electrode and the EA from Al electrode. For all cyclic voltammetry, electrolyte solution of 0.1 M Bu_4NClO_4 in acetonitrile was used. A three-electrode compartment electrochemical cell consisted of an ITO or Al glass electrode as the working electrode in sample prepared, a platinum wire (0.8 mm) as the counter electrode, and Ag/AgCl as the reference electrode [16]. The cyclic voltammograms were obtained at a scan rate of 400 mV/sec. The electrochemical gap (E_g), electron affinity (EA) and ionization potential (IP) of the films containing Benzoxazole dendrimer were investigated using cyclic-voltammetry (C-V). To transpose the measured redox behavior into estimates for the IP and EA, it is necessary to obtain the electrochemical potentials relative to the vacuum level, where IP and EA are also defined. An empirical relationship has been proposed by Bredas *et al.* [17]. It was found that the film of dendrimers could be irreversibly oxidized and reduced. The cyclic voltammogram of 1st generation Benzoxazole dendrimer is shown in Figure 3. The oxidation onset potential and the reduction onset potential of Benzoxazole dendrimer



G1-4BO (Mw: 1422.16)

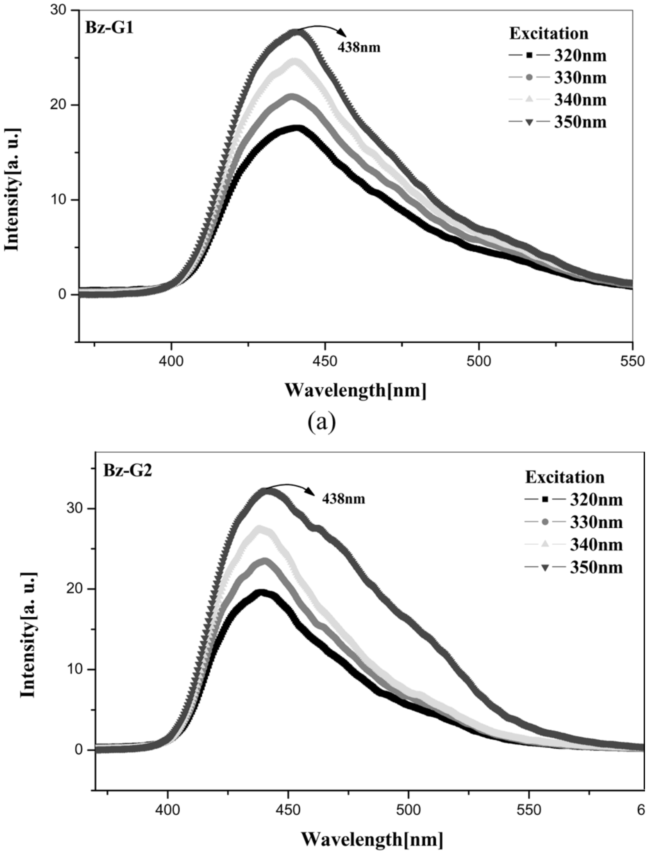
(a)



G2- 8BO (Mw: 3132)

(b)

FIGURE 1 The chemical structures of (a) 1st and (b) 2nd generation benzoxzole dendrimer.



(a)

(b)

FIGURE 2 PL spectra of (a) 1st and (b) 2nd generation Benzoxzole dendrimer.

were then measured to be +2.05 V and −1.64 V. IP, EA, and E_g are 6.85 eV, 3.16 eV, and 3.69 eV.

The Benzoxazole dendrimers were characterized by photoluminescence (PL) spectra. The photoluminescence (PL) spectra were measured using Perkin-Elmer LS45 luminescence spectrometer. The spectra featuring the PL of dendrimers were shown in Figure 2. The PL peaks of dendrimers were observed at the wavelength of 438 nm. The peak wavelength of 438 nm was in the blue region.

The organic materials were successively evaporated on top of ITO substrate under 5×10^{-6} torr with deposition rate of about 1.0 Å/s. Metal cathode was deposited under 5×10^{-6} torr with the deposition

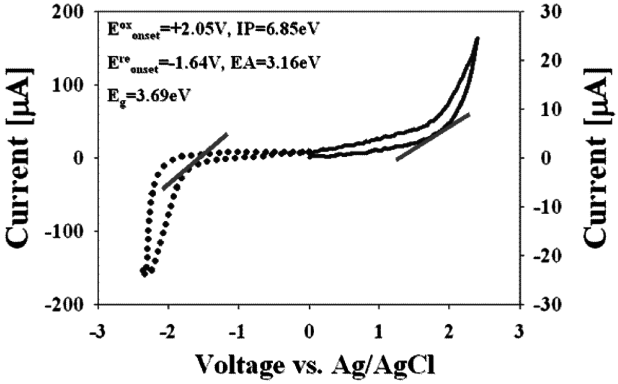


FIGURE 3 Cyclic voltammogram of Benzoxzole dendrimer.

rate of about 10 Å/s (Li:Al). The emission areas of each device were $3 \times 3\,\text{mm}^2$. The device structures were fabricated with this film as shown in Figure 4, where one device structure is (a) ITO/PVK dispersed 1st generation Benzoxazole dendrimer/Li:Al and the other one is (b) ITO/PVK:PBD dispersed 2nd generation Benzoxazole dendrimer/Li:Al. The blend layers were spin coated onto the ITO glass for device. Current density-voltage (J-V) and luminance-voltage (L-V) characteristics were measured using Flat Panel Display Analysis System (Model 200-AT).

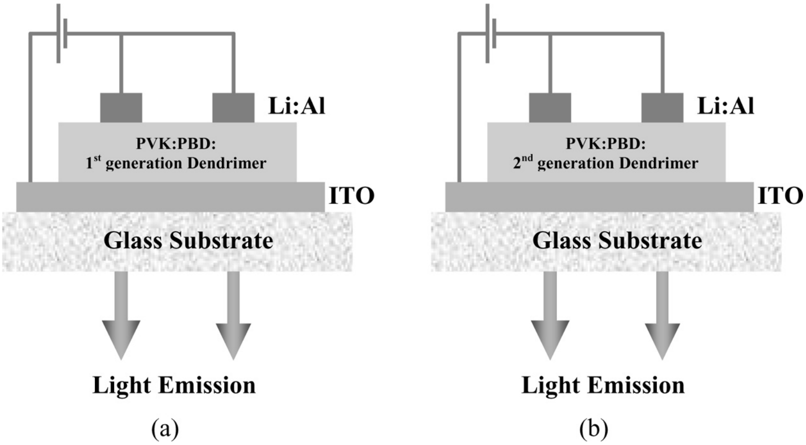


FIGURE 4 The structures of (a) device I and (b) device II.

III. RESULT AND DISCUSSION

Gn-mBO type dendrimers were prepared according to the modification of the previous report [18].

G1-4BO: The mixed 25 ml of toluene solution of 0.38 g (1.82 mmol) of 2-(2-hydroxypenyl)Benzoxazole and 0.21 g (1.82 mmol) of TMEDA were slowly added to 0.30 g (0.41 mmol) of G1-4Cl at room temperature. The reaction mixture was stirred at 50°C for 2 hrs. The salt and excess reactants were removed by chromatography by using mixed solvent THF and toluene (3 to 7 respectively) and silicagel column. Yield: 0.42 g (0.30 mmol, 72%) as light yellow solid. ^{1}H-NMR (ppm, $CDCl_3$): $\delta = 0.05$ (s, 12H, SiMe, G0), 0.22 (s, 24H, SiMe, G1), $0.35 \sim 0.68$, $0.68 \sim 0.84$ (m, 16H, CH_2, G0), $6.85 \sim 7.02$, $7.02 \sim 7.22$, $7.22 \sim 7.48$, $7.48 \sim 7.67$, $7.67 \sim 7.83$, $7.05 \sim 8.20$ (BO). ^{13}C-NMR (ppm, $CDCl_3$): $\delta = -2.20$ (SiMe, G0), -1.55 (SiMe, G1), 8.22 (CH_2, G0), 110.29, 119.89, 121.19, 121.44, 121.73, 124.27, 124.77, 131.08, 132.43, 141.73, 150.46, 154.39, 162.19 (BO). Anal. calcd. for $C_{72}H_{84}O_{12}Si_8N_4$ (Mw = 1,422): C, 60.75%, H, 5.90%, N, 3.94%, Found: C, 60.24%, H, 6.02%, N, 3.90%. GPC: $Mw/Mn = 1.00$ (2402/2397), Rt = 18.32 min.

G2-8BO: The preparation and purification of G2-8BO used the same methods as the preparation of G1-4BO. The reaction was carried out with 0.32 g (1.52 mmol) of 2-(2-hydroxypenyl)Benzoxazole, 0.17 g (1.52 mmol) of TMEDA, and 0.30 g (0.17 mmol) of G2-8Cl. Yield: 0.40 g (0.13 mmol, 76%) as light yellow solid. ^{1}H-NMR (ppm, $CDCl_3$): $\delta = 0.05$ (s, 24H, SiMe, G0 $\sim$ G1), 0.21 (s, 48H, SiMe, G2), $0.40 \sim 0.68$, $0.68 \sim 0.90$, $1.42 \sim 1.84$ (m, 48H, CH_2, G0 $\sim$ G1), $3.52 \sim 3.77$ (m, 32H, OCH_2, G1), $6.87 \sim 7.04$, $7.04 \sim 7.20$, $7.26 \sim 7.50$, $7.50 \sim 7.66$, $7.66 \sim 7.85$, $8.08 \sim 8.20$ (BO). ^{13}C-NMR (ppm, $CDCl_3$): $\delta = -4.38$ (SiMe, G0 $\sim$ G1), -1.48 (SiMe, G2), 4.76, 8.10 (CH_2, G0) 12.61, 25.91 (CH_2, G1), 64.99 (OCH_2, G1), 110.34, 119.90, 121.21, 121.51, 121.81, 124.27, 124.79, 131.04, 132.45, 141.75, 150.47, 154.27, 162.09 (BO). Anal. calcd. for $C_{160}H_{200}O_{28}Si_{16}N_8$ (Mw = 3,132): C, 61.30%, H, 6.38%, N, 3.57%, Found: C, 60.98%, H, 6.02%, N, 3.54%. GPC: $Mw/Mn = 1.00$ (2926/2915), Rt = 17.65 min.

The EL spectra of the devices are shown in Figure 5. The peak of device I, II was observed at the wavelength of 441 nm and 447 nm, respectively. The emission wavelength of devices was in the blue region same as PL. Figure 6 shows the current density-voltage and luminance-voltage characteristics of device I and II. The current density of device I and II were observed 15.65 mA/cm^2 and 17.66 mA/cm^2 at 10 V, respectively. Also, the luminance of device I and II were observed 52 cd/m^2 and 57 cd/m^2 at 10 V, respectively. This value is

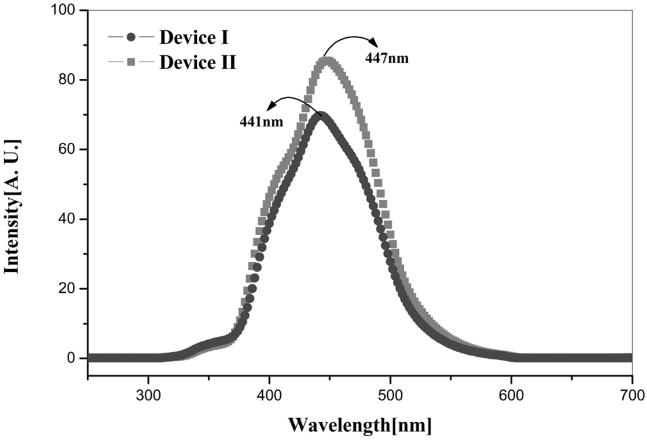


FIGURE 5 EL spectra of device I and II.

much lower than other small molecules but we expect that when the generation increases this electroluminescent properties will be increased. Figure 7 shows the luminescence efficiency-luminance characteristics of devices I and II. The luminescence efficiency of device I and II were found to be 0.12 lm/W and 0.1 lm/W. We found that generation number can have a small effect on device efficiency.

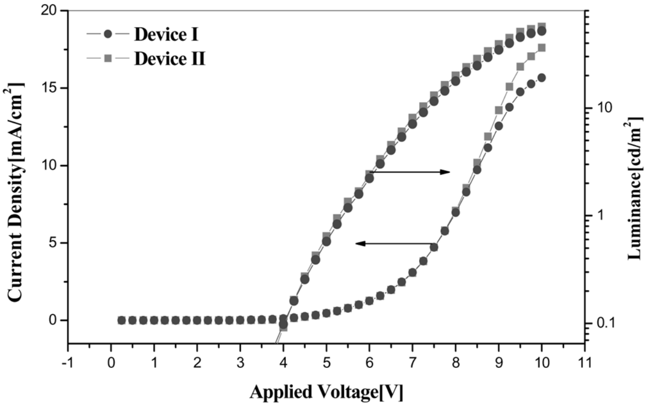


FIGURE 6 Current density-voltage and luminance-voltage characteristics of device I and II.

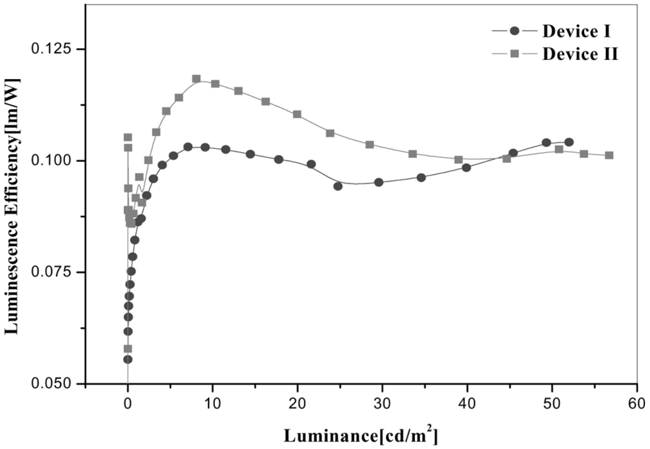


FIGURE 7 Luminescence efficiency of device I and II.

IV. CONCLUSION

We synthesized Benzoxazole dendrimers as light emitting materials. We obtained the pure dendrimers from the information of NMR, GPC, and elemental analysis. Light-emitting devices based dendrimer as emitter have been fabricated and investigated in structure of ITO/PVK:PBD dispersed Benzoxazole dendrimers/Li:Al, in which PVK is used as the hole transporter and PBD as electron transporter. We found that the emission wavelength of devices was in the blue region same as PL. The luminance of device I and II were observed 52 cd/m^2 and 57 cd/m^2 at 10 V, respectively. This value is much lower than other polymers and small molecules but we expect that when the generation increases this electroluminescent properties will be increased. The experiments about variation of demdrimers generation are in progress.

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