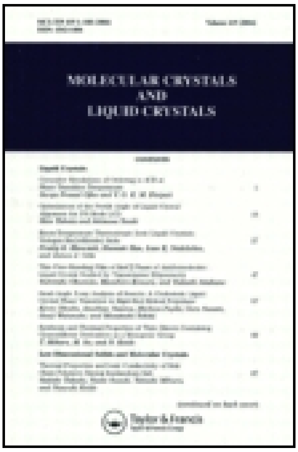

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Synthesis and Characterization of Thermally Cross-Linkable Oligophenothiazine

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A series of 10-butylphenothiazine trimer (3-PTVB) and pentamer (5-PTVB) with in-situ *thermally cross-linkable vinyl benzene were synthesized successfully. The TGA thermograms revealed that 3-PTVB and 5-PTVB were stable up to 430 and 370 °C, respectively. In the first heating scan of DSC thermograms, 3-PTVB and 5-PTVB showed glass transition temperature (T_g) at 113 °C and 95.3 °C (143 °C). Both 3-PTVB and 5-PTVB showed broad endothermic process in the region of 185–220 °C, which is thermally cross-linking temperature. In the second heating process, Tg and endothermic process were not observed. Wavelength of UV-visible maximum absorption of thermally cured 3-PTVB is 340 nm, which is same as the UV-visible maximum absorption of 5-PTVB. The thermally cured films showed no damage nor any discernible change in the UV-visible spectrum after washing with organic solvents such as methylene chloride (MC), chloroform, and toluene. Thermally cured 3-PTVB and 5-PTVB films were electrochemically very stable. The HOMO energy level of 3-PTVB and 5-PTVB were −4.98 and −4.86 eV, respectively. Double layer structured polymer light-emitting diodes based on* in-situ *thermally cured 3-PTVB and 5-PTVB were fabricated. The maximum luminance efficiency of devices based on 3-PTVB and 5-PTVB were 1.004 cd/A at 14.0 V and 1.074 cd/A at 16.5 V, respectively, which are much higher than that of the device without thermally cured 3-PTVB or 5-PTVB (0.348 cd/A at 15.0 V).*

Keywords *in-situ* thermally curable oligomer; phenothiazine; *p*-type organic semiconductor; Hole injection material

1. Introduction

Conjugated polymers have been studied in polymer light-emitting diodes (PLEDs) [1–4], polymer solar cells (PSCs) [5–7], thin film transistors (TFTs) [8–13], and electrochromic devices (ECDs) [14,15] Among these, PLEDs and PSCs have been focused tremendously because of easiness of process. To get highly efficient devices, multi-layer structured devices are fabricated with charge (hole and electron) injection and transporting layer. The charge (hole and electron) injection and transporting processes are crucial factors for improving the performances of polymer light-emitting diodes (PLEDs) and polymer solar cells (PSCs). In order to fabricate multi-layer structured device, the hole injection/transporting layer should have good solvent resistance to successive layer coating. Recently, *in-situ* thermally

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*Address correspondence to Joo Hyun Kim, Department of Polymer Engineering, Pukyong National University, Yongdang-Dong, Nam-Gu, Busan 608-739, Korea. Tel: 82–51-629-6452, Fax: 82–51-629-6429. E-mail: jkim@pknu.ac.kr polymerizable hole injection materials based on triarylamine, alkylphenothiazine, alkylcarbazole have been studied [16–23]. The devices based on reported hole injection materials exhibited excellent performances.

Poly(10-hexyl-10*H*-hexylphenothiazin-3,7-diyl) (PT) is well known very strong electron donor and has high-lying ionization potential so that PT can be used as hole injection material [24,25]. In our previous report [22], PT with *in-situ* thermally polymerizable methyl methacrylate showed good hole injection properties. However, lacks of reproducibility in polymerization reaction and purification process were problem. The purification and reproducibility in the synthesis of oligomers such as trimer or pentamer are much easier than those of analogues' polymers. Here, we report the synthesis and physical properties of trimer and pentamer of 10-butylphenothiazine with *in-situ* polymerizable vinyl benzene.

2. Experimental Section

2.1 Materials and Synthesis

Tetrahydrofuran (THF) was distilled over sodium/benzophenone. Methylene chloride (MC) was distilled over CaH_2. All other chemicals were purchased from Sigma-Aldrich Co, Tokyo Chemical Industry (TCI) or Alfa Aesar (A Johnson Matthey Company) and were used as received unless otherwise described.

2.1.1. ***7-[4-(4-vinyl-benzyloxy)-phenyl]-{7′-[4-(4-vinyl-benzyloxy)-phenyl]-10-butyl-10H-phenothiazine-3-yl}-10,10′-dibutyl-10H,10′H-3,3′-biphenothiazine (3-PTVB)****.* A solution of 4-vinyl benzyl chloride (64.0 mg, 0.420 mmol) was added dropwise to a portion of compound **1**[26] (150 mg, 0.170 mmol) and potassium carbonate (580 mg, 0.420 mmol) in DMF (20 mL) under nitrogen atmosphere at 40 °C. After stirring for overnight, a portion of 50 mL of water was added to the reaction mixture and extracted three times with EA. The combined organic layer was dried over anhydrous $MgSO_4$ and evaporation the solvent using a rotary evaporator. The crude product was purified by recrystallization using methanol/MC. The yield of yellow solid is 87.1% (0.17 g). mp: 211.3 °C. MS (MALDI-TOF): $[M\text{-}H]^+$, m/z 1176.8. ^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ 7.43~7.42 (b, 14H), 7.33~7.31 (b, 10H), 7.01~7.00 (d, J = 8.8 Hz, 4H), 6.88 (b, 4H), 6.77~6.70 (dd, J_1 = 17.6 Hz, J_2 = 11.0 Hz, 2H), 5.79~5.75 (dd, J_1 = 17.6 Hz, J_2 = 0.7 Hz, 2H), 5.28~5.25 (dd, J_1 = 11.0 Hz, J_2 = 0.7 Hz, 2H), 5.08 (s, 4H), 3.90~3.87 (t, J = 6.9 Hz, 6H), 1.86~1.79 (m, 6H), 1.54~1.45 (m, 6H), 0.99~0.95 (t, 9H), ^{13}C-NMR (100 MHz, $CDCl_3$, ppm): δ 158.05, 144.06, 143.98, 143.79, 137.33, 136.52, 136.43, 135.10, 134.29, 134.24, 132.91, 127.66, 127.52, 126.43, 125.45, 125.23, 125.16, 115.62, 115.40, 115.15, 114.08, 69.85, 47.21, 29.69, 28.98, 20.20, 13.84. Anal. Calcd. for $C_{78}H_{71}N_3O_2S_3$: C, 79.49; H, 6.07; N, 3.57; O, 2.71; S, 8.16. Found: C, 77.31; H, 4.044; N, 6.337; S, 10.41.

2.1.2. ***3,6-bis-{10,10′-dibutyl-7′-[4-(4-vinyl-venzyloxy)-phenyl]-10H,10H′-[3,3′]biphenothiazinyl}-10-hexyl-10H-phenothiazine (5-PTVB)****.* A solution of 4-vinyl benzyl chloride (32.0 mg, 0.210 mmol) was added dropwise to a portion of compound **2**[26] (100 mg, 0.070 mmol) and potassium carbonate (290 mg, 0.210 mmol) in DMF (20 mL) under nitrogen atmosphere at 40 °C. After stirring for overnight, a portion of 50 mL of water was added to the reaction mixture and extracted three times with EA. The combined organic layer was dried over anhydrous $MgSO_4$ and evaporation the solvent using a rotary evaporator. The crude product was purified by recrystallization using methanol/MC. The yield of yellow solid is 71.8% (0.086 g). mp: 131.2 ºC. MS (MALDI-TOF): $[M\text{-}H]^+$, m/z 1712.3. ^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ 7.45∼7.41 (m, 14H), 7.31 (b, 20H), 7.02∼7.00 (d, $J = 8.8$ Hz, 6H), 6.89 (b, 6H), 6.73 (dd, $J_1 = 17.6$ Hz, $J_2 = 11.0$ Hz, 2H), 5.79∼5.74 (dd, $J_1 = 17.6$ Hz, $J_2 = 1.1$ Hz, 2H), 5.27∼5.25 (dd, $J_1 = 11.0$ Hz, $J_2 = 0.7$ Hz, 2H), 5.08 (s, 4H), 3.91∼3.88 (t, $J = 6.9$ Hz, 10H), 1.87∼1.79 (m, 10H), 1.52∼1.47 (m, 14H), 0.99∼0.95 (t, $J = 7.4$ Hz, 15H), ^{13}C-NMR (100 MHz, $CDCl_3$, ppm): δ 158.04, 144.02, 143.94, 143.75, 137.31, 136.51, 136.43, 135.05, 134.23, 132.87, 127.65, 127.50, 126.41, 125.44, 125.22, 125.13, 124.76, 124.70, 115.40, 115.14, 114.07, 69.82, 47.55, 47.19, 31.47, 28.96, 26.83, 26.67, 22.60, 20.19, 14.01, 13.84. Anal. Calcd. for $C_{112}H_{105}N_5O_2S_5$: C, 78.51; H, 6.18; N, 4.09; O, 1.87; S, 9.36. Found: C, 80.06; H, 4.577; N, 6.066; S, 10.36.

2.2. Device Fabrication

ITO-coated glass substrates were cleaned with deionized water, acetone, methanol, 2-propanol in ultrasonic bath. A solution of 3-PTVB or 5-PTVB (5 mg/mL in chloroform:chlorobenzene (1:1 by volume)) layer was spin-coated as a hole injection layer (HIL) onto the ITO. Before spin-coating, 3-PTVB or 5-PTVB was filtered through 0.20-μm PTFE syringe filter. After spin coating, the thin film was heated up to 185 °C for 2 hours. The typical thickness of 3-PTVB or 5-PTVB film was 5 ∼ 10 nm. The green emitting polymer (PF9B)^{27} were dissolved in toluene and filtered through 0.20-μm PTFE syringe filter before spin coating. The typical thickness of emissive layer was 60 nm. Al was evaporated as cathode onto the surface of the emissive polymer film by thermal evaporation technique at 2.0×10^{-6} torr. The typical active area of the devices was 6 mm^2.

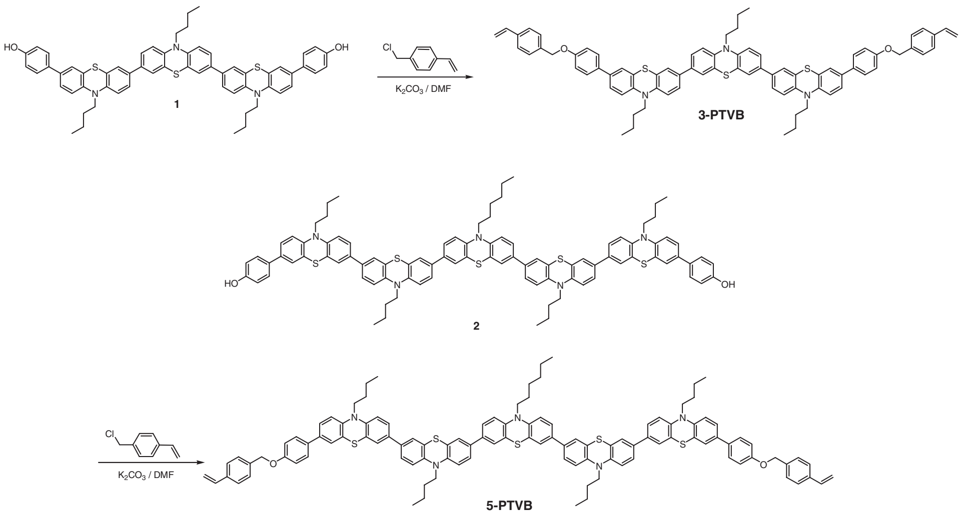
2.3. Measurements

Synthesized compounds were characterized by ^{1}H-NMR and ^{13}C-NMR spectrum, which were obtained with a JEOL JNM ECP-400 spectrometer. The elemental and MASS analyses of synthesized compounds were carried out on a Elementar Vario macro/micro elemental analyzer and Shimadzu GC-MS QP-5050A spectrometer. Thermogravimetric analysis (TGA) was carried out under nitrogen atmosphere at a heating rate of 10 °C/min with a Perkin-Elmer TGA 7 thermal analyzer. Differential scanning calorimetry (DSC) was measured by a Perkin Elmer (Pyris 1, Diamond) under nitrogen atmosphere at a scan rate of 10 °C/min. UV-Visible spectrum were recorded using a JASCO V-530 UV/VIS Spectrophotometer. Cyclic voltammetry was performed by a EG&G 362 Scanning Potentiostat with a three electrode cell in a solution of Bu_4NPF_6 (0.1 M) in freshly distilled methylene chloride at a scan rate of 100 mV/s. Pt wires were used as the counter and working electrode and a Ag/Ag^+ electrode was used as the reference electrode. Prior to each measurement, the cell was deoxygenated with argon. The current density-voltage-brightness (J-V-B) characteristics were measured using a source meter (KEITHLEY 2400) and a luminometer (Minolta LS110).

3. Results and Discussion

3.1 Synthesis and Characterization of oligomers

Scheme 1 shows the synthetic procedures for thermally cross-linkable phenothiazine (PT) trimer and pentamer, which are synthesized by the well-known palladium-catalyzed Suzuki coupling reaction between brominated PT and borylated PT to extend length of



Scheme 1. Synthesis of thermally cross-linkable 10*H*-butylphenothiazine oligomers.

π-conjugation. All the compounds were well characterized by elemental analysis, MASS, ^{1}H-NMR, and ^{13}C-NMR.

Figure 1 shows the TGA thermaograms of 3-PTVB and 5-PTVB. Phenothiazine trimer and pemtamer with vinyl benzene (VB) are thermally stable because points of 5%-weight loss in TGA thermogram of 3-PTVB and 5-PTVB appear at 403 and 370 °C, respectively. In order to investigate, thermal behavior of 3-PTVB and 5-PTVB, we performed differential scanning calorimetry (DSC). As shown in Figure 2 (a), in the first heating scan, glass transition temperature (T_g) of 3-PTVB shows at 113 °C and 3-PTVB shows broad endothermic process in the region of 185–220 °C with a peak at 217 °C. In the second heating process, 3-PTVB does not have T_g and endothermic process, because the thermally curing reaction is completed in the first heating scan. From the DSC thermogram one can easily notice that the endothermic process at 217 °C in the first scan is due to thermally cross-linking reaction of VB group. In the first heating scan of 5-PTVB, it shows endothermic process in the region of 183–213 °C with a peak at 200 °C. In the first scan of 5-PTVB seems to be show two glass transition processes at 95.3 and 143 °C. From the DSC thermogram,

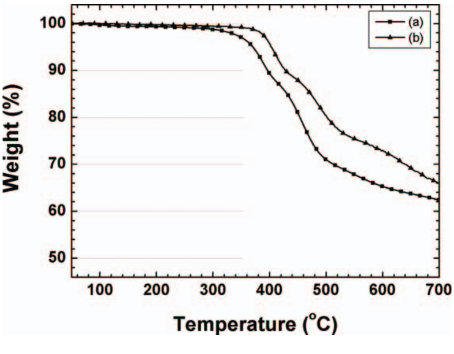


Figure 1. TGA thermorgrams of (a) 3-PTVB and (b) 5-PTVB.

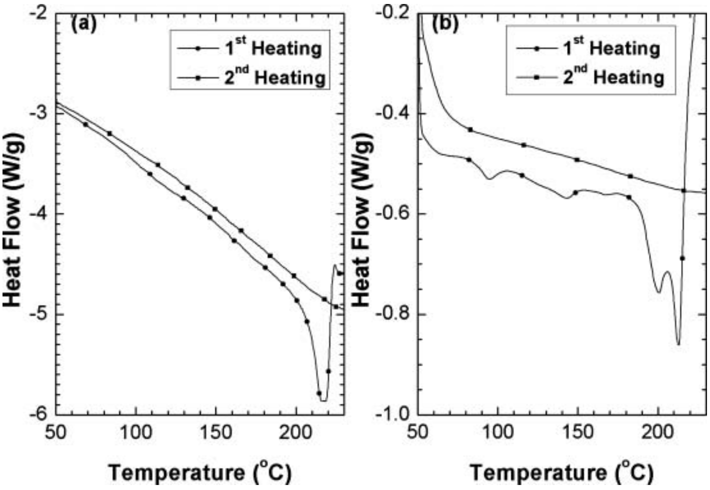


Figure 2. DSC thermorgrams of (a) 3-PTVB and (b) 5-PTVB.

we confirm that T_g of 5-PTVB is higher than that of 3-PTVB. We cannot observe the endothermic process in the second heating scan of 5-PTVB.

Figure 3 shows the UV-visible absorption spectrum of 3-PTVB and 5-PTVB. The absorbance of thermally cured 3-PTVB film was slightly decreased than that of pristine film, because the molecules in the cured film are more close-packed than pristine film. The absorbance of thermally cured 3-PTVB did not show big difference on washing with organic solvent such as MC. In the optical properties of 5-PTVB film, similar features were observed (Figure 3 (b)). Also, the shapes of the spectrum of before and after cured films were almost identical to those of pristine 3-PTVB and 5-PTVB films.

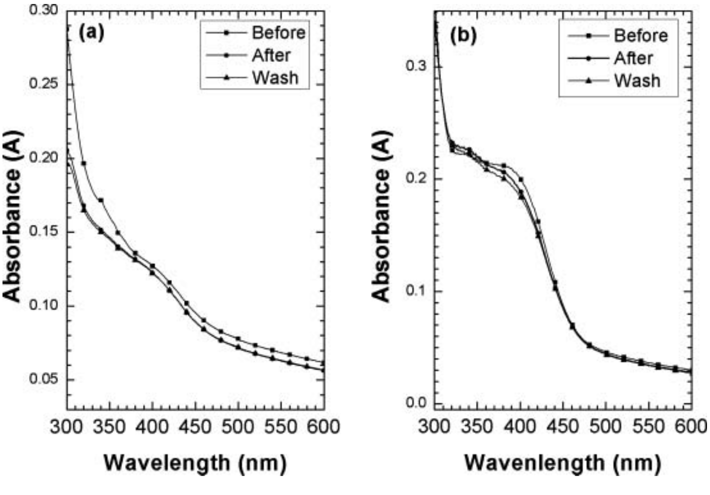


Figure 3. UV-Visible spectrum of (a) 3-PTVB and (b) 5-PTVB. (rectangular: before cross-link, triangle: after cross-link, circle: washed cross-linked film with MC)

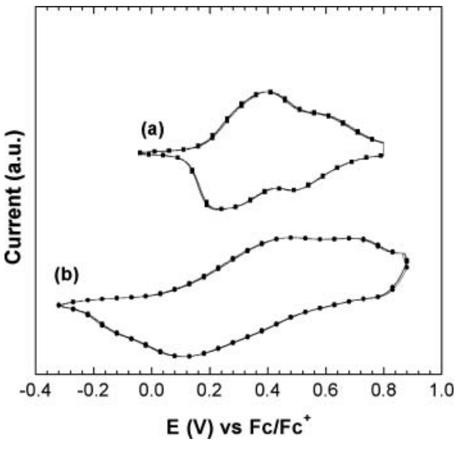


Figure 4. Cyclic voltammogram of thermally cross-linked (a) 3-PTVB and 5-PTVB film on ITO coated glass.

3.2 Electrochemical and electroluminescent properties

The HOMO energy levels were estimated from the oxidation onset potential by the energy level of ferrocene is – 4.8 eV. Cyclic voltammograms (CVs) of thermally cured 3-PTVB and 5-PTVB film on ITO coated glass show quasi-reversible behavior (Figure 4). Two oxidation peaks at 0.41 and 0.60 V vs. Fc/Fc^+ were observed in the CV of 3-PTVB (Figure 4 (a)). Also, the CV of 5-PTVB were observed two oxidation peaks at 0.40 and 0.71 V vs. Fc/Fc^+ were observed (Figure 4 (b)). The thermally cured 3-PTVB and 5-PTVB films on ITO don't change in the cathodic and anodic peak current upon repeated redox scans in 0.1 M Bu_4NPF_6 in MC. This is also indicating that cured 3-PTVB and 5-PTVB exhibit good electrochemical stability and solvent resistance. The HOMO energy level of cured 3-PTVB figured out –4.98 eV from the oxidation onset potential of the first scan of the CV, which is very similar to that of cured 5-PTVB film (-5.86 eV). This is very similar to that of poly(hexylphenothiazine)[24,25] and thermally cured poly(alkylphenothiazine)[22], whose HOMO energy level are $-4.9 \sim -5.0$ eV.

In order to investigate hole injection and transporting properties of cured 3-PTVB and 5-PTVB, we fabricated double layer structured device, ITO/cured 3-PTVB (10 nm)/PF9B (60 nm)/Al (device I, Figure 5 (b)) and ITO/cured 5-PTVB (10 nm)/PF9B (60nm)/Al (device II, Figure 5 (c)). The thickness of films was measured by Alpha-Step IQ surface

Table 1. Optical, electrochemical, and thermal properties of 3-PTVB and 5-PTVB.

	UV_{max} (nm)	E_{gap} (eV)	$E_{ox,peak}$ (V)	E_{onset} (V), HOMO (eV)[a]	T_d (°C)[b]	T_g (°C)[c]
Cured 3-PTVB	340	2.64	0.41, 0.60	0.18, −4.98	403	113
Cured 5-PTVB	340	2.67	0.40, 0.71	0.06, −4.86	370	95.3, 143

[a] estimated from the oxidation onset potential by the energy level of ferrocene is – 4.8 eV
[b] the point of 5%-weight loss, measured using uncured oligomer
[c] measured using uncured oligomer

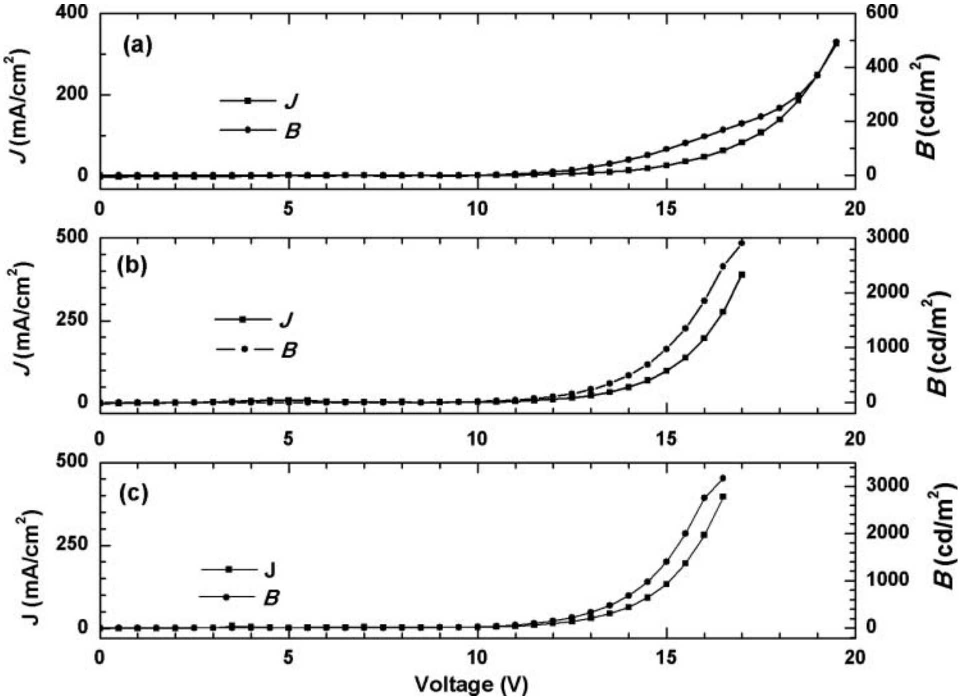


Figure 5. I-V-L curves of the device (a) ITO/PF9B/Al, (b) ITO/cured 3-PTVB/PF9B/Al, and (c) ITO/cured 5-PTVB/PF9B/Al.

profiler. Figure 5 shows current density (*J*) and brightness (*B*) as a function of applied voltage (V) of the device I and device II. The device performances are summarized in Table 2. The *J*-V curves of the devices show typical rectification properties. The turn-on voltage (defined as the voltage required to give a luminescent of 1 cd/m^2) of the device I and II were 7.5 V. In order to compare the performances with device I and device II, we also fabricated the device without cured 3-PTVB or 5-PTVB (ITO/PF9B/Al, Figure 5 (a)). The turn-on voltage of device without cured 3-PTVB or 5-PTVB was 9.5 V, which was much

Table 2. Device performances of LEDs prepared with thermally cured 3-PTVB and 5-PTVB.

	V_{on} (V)[a]	LE_{100} (cd/A)[b]	LE_{max} (cd/A)[c]	B_{max} (cd/m^2)[d]
ITO/PF9B/Al	9.5	0.372 @ 14.0 V	0.348 @ 15.0 V	496 @ 15.0 V
ITO/cured 3-PTVB/PF9B/Al	7.5	0.844@ 12.0 V	1.004@ 14.0 V	2906@ 17.0 V
ITO/cured 5-PTVB/PF9B/Al	7.5	0.972@ 11.5 V	1.074@ 13.5 V	3165@ 16.5 V

[a] defined as the voltage required to give a luminescent of 1 cd/m^2.

[b] luminance efficiency at 100 cd/m^2.

[c] maximum luminescence efficiency.

[d] maximum brightness

higher than device I and device II. The maximum brightness and maximum efficiency of device I and device II were dramatically improved than the device without cured 3-PTVB or 5-PTVB. From the electroluminescent properties, cured 3-PTVB and 5-PTVB show good hole injection and transporting properties. In addition, the maximum luminescence efficiency and brightness of device II were 1.074 cd/A and 3165 cd/m^2, which were higher than those of device I (1.004 cd/A and 2906 cd/m^2). Because cured 5-PTVB has longer π-conjugation length compared to that of cured 3-PTVB.

4. Conclusions

We synthesized new π-conjugated trimer (3-PTVB) and pentamer (5-PTVB) based on 10-butylphenothiazine with vinyl benzene as thermally cross-linkable unit by well known palladium catalyzed the Suzuki reaction. From the UV-Visible spectroscopy, thermally cured 3-PTVB and 5-PTVB are safe to the successive layer coating by the solution process. Also, we confirm that the cured oligomers are electrochemically stable. The performances of double layer structured devices exhibited superior performances than those of the device without 3-PTVB or 5-PTVB. In addition, turn-on voltages of the device based on cured oligomers were much lower than that of the device without cured oligomers. From the results, thermally cured 3-PTVB and 5-PTVB are potential materials for hole injection/transporting layer.

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