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In-situ Thermally Curable Hyper-branched 10*H*-butylphenothiazine

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A hyper branched 10-butylphenothiazine with in-situ thermally curable methacrylate (1,3,5-tris-[{10-Butyl-3-(4-(2-methyl-acryloyloxy)-phenyl)-7-yl-10*H*-phenothiazine}]-benzene, (tris-PTMA)) was synthesized successfully. From the TGA thermogram of tris-PTMA was thermally stable up to 336 ºC. In the first heating scan of DSC thermogram, tris-PTMA showed glass transition temperature (T_g) at 140 ºC and broad endothermic process in the region of 144-179 ºC, which is thermally curing temperature. In the second heating process, T_g exhibited at 158.7 ºC and endothermic process was not observed. Thermally cured tris-PTMA showed no big change in the UV-visible spectrum after washing with organic solvent such as methylene chloride, chloroform, toluene, indicating that thermally cured film was very good solvent resistance. Thermally cured tris-PTMA was electrochemically stable and the HOMO energy level of tris-PTMA was −5.54 eV. The maximum luminance efficiency of double layer structured polymer light-emitting diode based on *in-situ* thermally cured tris-PTMA was 0.685 cd/A at 16.0 V, which was higher than that of the device without thermally cured tris-PTMA (0.348 cd/A at 15.0 V).

Key Words : *In-situ* thermal curing, Hyper branched 10*H*-butylphenothiazine, *p*-Type organic semiconductor, Hole transporting/injection material

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] 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 important factors for improving the performances of PLEDs and PSCs. In order to fabricate multi-layer structured device, the hole injection/transporting layer should have good solvent resistance to successive layer coating. There have been extensive studies to make hole injection/transporting materials mainly focused on thermally curable materials, because insoluble layers are easily obtained *via in-situ* thermally curable reaction of solution deposited films. Recently, *in-situ* thermally polymerizable hole injection materials based on triarylamine, alkylphenothiazine, alkylcarbazole[16-24] have been developed. 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 PT can be used as hole injection material.[25,26] In our previous report,[23] 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 are easier than those of polymers. Here, we report the synthesis and physical properties of hyper branched 10-butylphenothiazine with *in-situ* polymerizable methacrylate.

Experimental Section

Materials. 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.

10-Butyl-10*H*-phenothiazine (1). A portion of 100 mg of benzyltriethylammonium chloride and 100 mL of 50 wt % aqueous NaOH were added to a solution of 30.0 g (0.150 mol) of 10*H*-phenothiazine in 100 mL of dimethyl sulfoxide (DMSO). The reaction mixture was stirred for 30 min. A portion of 28.8 g (0.210 mol) of 1-bromobutane was added to the reaction mixture and then stirred for 12 hours at room temperature. The reaction mixture was neutralized with aqueous HCl (35 wt %) and extracted three times with 100 mL of ethyl acetate (EA). The combined organic layer was dried over anhydrous magnesium sulfate and the organic solvent removed using a rotary evaporator. The crude liquid product was purified by flash column chromatography using n-hexane. The yield of light yellow liquid was 36.2 g (94.3%). MS: [M^+], *m/z* 255. ^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ 7.18-7.14 (m, 4H), 6.94-6.86 (m, 4H), 3.88-3.84 (t, *J* = 7.3 Hz, 2H), 1.84-1.77 (m, 3H), 1.52-1.42 (m, 2H), 0.97-

0.94 (t, J = 7.3 Hz, 3H), ^{13}C-NMR (100 MHz, $CDCl_3$, ppm): δ 145.10, 127.20, 126.99, 124.68, 122.12, 115.22, 46.79, 28.78, 20.00, 13.72. Anal. Calcd. for $C_{16}H_{17}NS$: C, 75.25; H, 6.71; N, 5.48; S, 12.56. Found: C, 75.92; H, 6.62; N, 5.58; S, 12.67.

3,7-Dibromo-10-butyl-10*H*-phenothiazine (2). A potion of 58.6 g (0.330 mol) of *N*-bromosuccinimide (NBS) in 100 mL of *N,N'*-dimethylformamide (DMF) was added dropwise to a solution of compound **1** (35.0 g, 0.140 mol) in 50 mL of DMF under the nitrogen atmosphere at 5 °C then stirred for 30 min. The reaction mixture was stirred for 5 hours at room temperature. A potion of 200 mL of water was added into the reaction mixture then extracted three times with 100 mL of EA. The combined organic layer was washed with aqueous sodium bisulfite (10 wt %) and then dried over anhydrous $MgSO_4$. The solvent was removed using a rotary evaporator. The crude product was purified by column chromatography on silica gel using *n*-hexane. The yield of yellow liquid was 45.1 g (79.7%). MS: [M^+], *m/z* 413. ^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ 7.24-7.21 (m, 4H), 6.69-6.67 (d, J = 8.8 Hz, 2H), 3.77-3.74 (t, J = 6.9 Hz, 2H), 1.76-1.69 (m, 2H), 1.47-1.37 (m, 2H), 0.94-0.90 (t, J = 7.3 Hz, 3H), ^{13}C-NMR (100 MHz, $CDCl_3$, ppm): δ 143.91, 129.95, 129.49, 126.21, 116.49, 114.57, 47.08, 28.55, 19.93, 13.71. Anal. Calcd. for $C_{16}H_{15}Br_2NS$: C, 46.51; H, 3.66; Br, 38.68; N, 3.39; S, 7.76. Found: C, 45.39; H, 3.624; N, 3.447; S, 7.624.

2-(4-Methoxy-phenyl)-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane (3). A portion of 38.5 mL (52.0 mmol) of n-butyl lithium (1.35 M in hexane) was added dropwise to a solution of 1-bromo-4-methoxy-benzene (7.50 g, 40.1 mmol) in 150 mL of THF under nitrogen atmosphere at −78 °C. The reaction mixture was stirred for 2 hours at −78 °C. A portion of 10.0 g (53.9 mol) of 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane was added into the reaction mixture at -78 °C. Then, the resulting mixture was allowed to warm up to room temperature and stirred for 12 hours. A portion of 100 mL of water was added to the reaction mixture slowly and extracted three times with 100 mL of EA. The combined organic layer was dried over anhydrous $MgSO_4$. The organic solvent removed using a rotary evaporator. The crude product was purified by flash column chromatography using MC/*n*-hexane (7/3). The yield of yellow liquid was 8.67 g (92.6%). MS: [M^+], *m/z* 234. ^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ 7.77-7.74 (d, J = 8.8 Hz, 2H), 6.91-6.88 (d, J = 8.5 Hz, 2H), 3.82 (s, 3H), 1.33 (s, 12H), ^{13}C-NMR (100 MHz, $CDCl_3$, ppm): δ 161.96, 136.33, 113.06, 83.23, 54.71, 24.63. Anal. Calcd. for $C_{13}H_{19}BO_3$: C, 66.70; H, 8.18; B, 4.62; O, 20.50. Found: C, 66.57; H, 8.28.

General Procedure of the Suzuki Coupling Reaction. A mixture of aryl bromide, aryl boronic ester, 3.0 mol % of tetrakis(triphenylphosphine) palladium[$Pd(PPh_3)_4$], and several drops of aliquat 336 in degassed 1:1 (by volume) mixed solvent of THF and 2 M K_2CO_3 was stirred for 12 hours at 75 °C under the nitrogen atmosphere. A portion of water was added to the reaction mixture and then extracted several times with EA. The combined organic layer dried over anhydrous $MgSO_4$. The solvent was removed by the evaporation under reduced pressure.

3-Bromo-10-butyl-7-(4-methoxy-phenyl)-10*H*-phenothiazine (4). Compound **4** was synthesized by the general procedure of the Suzuki coupling reaction between 6.57 g (15.9 mmol) of compound **2** and 3.72 g (15.9 mmol) of compound **3**. The crude product was purified by flash column chromatography using MC/*n*-hexane (3/7). The yield of yellow solid was 4.40 g (62.7%). MS: [M^+], *m/z* 441. mp 88.9 °C. ^{1}H-NMR (400 MHz, DMSO-d_6, ppm): δ 7.57-7.55 (d, J = 8.8 Hz, 2H), 7.46-7.44 (dd, J_1 = 8.4 Hz, J_2 = 2.2 Hz, 1H), 7.39-7.38 (d, J = 1.8 Hz, 1H), 7.36-7.34 (m, 2H), 7.08-7.06 (d, J = 2.5 Hz, 1H), 6.99-6.95 (m, 3H), 3.88-3.85 (t, J = 7.0 Hz, 2H), 3.78 (s, 3H), 1.39-1.62 (m, 2H), 1.44-1.35 (m, 2H), 0.90-0.86 (t, J = 7.0 Hz, 3H), ^{13}C-NMR (100 MHz, $CDCl_3$, ppm): δ 158.89, 144.32, 143.50, 135.42, 132.34, 129.82, 129.58, 127.48, 126.74, 125.61, 125.41, 124.36, 116.39, 115.60, 114.29, 114.15, 55.30, 47.15, 28.76, 20.08, 13.79. Anal. Calcd. for $C_{23}H_{22}BrNOS$: C, 62.73; H, 5.04; Br, 18.14; N, 3.18; O, 3.63; S, 7.28. Found: C, 62.91; H, 5.143; N, 3.220; S, 7.184.

10-Butyl-3-(4-methoxy-phenyl)-7-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)-10*H*-phenothiazine (5). A portion of 4.23 mL (10.7 mmol) of n-butyl lithium (2.5 M in hexane) was added dropwise to a solution of compound **4** (3.22 g, 7.83 mmol) in 100 mL of THF under the nitrogen atmosphere at −78 °C. The reaction mixture was stirred for 2 hours at −78 °C. A portion of 2.07 g (11.1 mmol) of 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane was added into the reaction mixture. Then, the resulting mixture was allowed to warm up to room temperature and stirred for 12 hours. A portion of 100 mL of water was added slowly to the reaction mixture and then the reaction mixture was extracted three times with 100 mL of EA. The combined organic layer was dried over anhydrous $MgSO_4$. The organic solvent removed using a rotary evaporator. The crude product was purified by flash column chromatography using EA/*n*-hexane (2/8) and recrystallization using methanol/MC. The yield of yellow solid was 2.63 g (67.8%). MS: [M+], *m/z* 487. mp 119.5 °C. ^{1}H-NMR (400 MHz, DMSO-d_6, ppm): δ 7.59-7.53 (d, J = 9.2 Hz, 2H), 7.50-7.48 (m, 2H), 7.37-7.34 (d, J = 5.5 Hz, 1H), 7.33 (d, J = 3.7 Hz, 1H), 7.06-6.97 (m, 4H), 3.91-3.88 (t, J = 7.0 Hz, 2H), 3.78 (s, 3H), 1.71-1.64 (m, 2H), 1.42-1.35 (m, 2H), 1.27 (s, 12H), 0.89-0.86 (t, J = 7.3 Hz, 3H), ^{13}C-NMR (100 MHz, $CDCl_3$, ppm): δ 159.04, 147.82, 143.48, 135.44, 133.86, 133.51, 132.66, 128.18, 127.11, 126.02, 125.25, 124.89, 123.67, 115.88, 114.82, 114.63, 83.82, 56.03, 54.83, 47.26, 28.23, 25.51, 20.25, 13.97. Anal. Calcd. for $C_{29}H_{34}BNO_3S$: C, 71.45; H, 7.03; B, 2.22; N, 2.87; O, 9.85; S, 6.58. Found: C, 71.93; H, 7.116; N, 2.94; S, 6.68.

1,3,5-Tris-[{10-butyl-3-(4-methoxy-phenyl)-7-yl-10*H*-phenothiazine}]-benzene (6). Compound **6** was synthesized by the general procedure of the Suzuki coupling reaction between 0.378 g (1.20 mmol) of 1,3,5-tribromobenzene and 1.93 g (3.96 mmol) of compound **5**. The crude product was purified by flash column chromatography using EA/*n*-hexane (2/8). The yield of yellow solid was 1.15 g (82.8%).

mp 274.4 °C. MS (MALDI-TOF): $[M-H]^+$, *m/z* 1155.4. ^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ 7.61(s, 3H), 7.48-7.45 (m, 12H), 7.34-7.32 (m, 6H), 6.96-6.90 (m, 12H), 3.93-3.90 (t, *J* = 5.8 Hz, 6H), 3.84 (s, 9H), 1.90-1.82 (m, 6H), 1.56-1.48 (m, 6H), 1.00-0.96 (t, *J* = 7.3 Hz, 9H), ^{13}C-NMR (100 MHz, $CDCl_3$, ppm): δ 158.92, 143.73, 141.01, 135.50, 132.60, 157.54, 126.08, 125.48, 123.51, 115.48, 114.18, 47.37, 29.68, 29.21, 20.21, 13.86. Anal. Calcd. for $C_{75}H_{69}N_3O_3S_3$: C, 77.89; H, 6.01; N, 3.63; S, 8.32. Found: C, 77.79; H, 6.11; N, 3.73; S, 8.29.

1,3,5-Tris-[{10-butyl-3-(4-hydroxy-phenyl)-7-yl-10*H*-phenothiazine}]-benzene (7). A portion of 6.16 mL (6.16 mmol) of BBr_3 (1 M in MC) was added dropwise to a solution of compound **6** (1.02 g, 0.878 mmol) in 50 mL of MC under the nitrogen atmosphere at 4 °C. The reaction mixture was allowed warm up to 35 °C and then was stirred for 5 hours. A portion of 100 mL of water was added to the reaction mixture and extracted three times with 50 mL of MC. The combined organic layer was dried over anhydrous $MgSO_4$. The solvent removed using a rotary evaporator. The crude product was purified by flash column chromatography using EA/MC/*n*-hexane (1/2/7 by vol.). The yield of yellow solid was 0.860 g (87.9%). mp 229.3 °C. MS (MALDI-TOF): $[M-H]^+$, *m/z* 1113.5. ^{1}H-NMR (400 MHz, DMSO-d_6, ppm): δ 9.49 (s, 3H), 7.78 (s, 3H), 7.71-7.69 (d, *J* = 7.3 Hz, 6H), 7.46-7.40 (m, 9H), 7.11-7.06 (m, 6H), 6.83-6.81 (d, *J* = 8.8 Hz, 6H), 3.96-3.92 (t, *J* = 6.9 Hz, 6H), 1.77-1.70 (m, 6H), 1.49-1.42 (m, 6H), 0.93-0. 90 (t, *J* = 7.3 Hz, 9H), ^{13}C-NMR (100 MHz, THF-d_8, ppm): δ 158.07, 145.57, 144.31, 141.92, 136.47, 136.03, 131.79, 127.97, 126.79, 126.43, 125.95, 125.83, 125.70, 125.58, 123.85, 120.00, 116.38, 116.32, 47.54, 29.82, 20.78, 14.13. Anal. Calcd. for $C_{72}H_{63}N_3O_3S_3$: C, 77.59; H, 5.70; N, 3.77; S, 8.63. Found: C, 77.67; H, 5.61; N, 3.87; S, 8.73.

1,3,5-Tris-[{10-butyl-3-(4-(2-methyl-acryloyloxy)-phenyl)-7-yl-10*H*-phenothiazine}]-benzene (tris-PTMA). A portion of triethylamine (0.160 g, 1.70 mmol) and 2-metha-acryloyl chloride (0.180 g, 1.70 mmol) were added dropwise to a portion of compound **7** (0.300 g, 0.262 mmol) in MC (20 mL) under nitrogen atmosphere at 0 °C. A portion of 100 mL of water was added to the reaction mixture and extracted three times with 50 mL of MC. The combined organic layer was dried over anhydrous $MgSO_4$. The solvent removed using a rotary evaporator. The crude product was purified by recrystallization using *n*-hexane/MC. The yield of yellow solid was 0.260 g (75.3%). mp 139.2 °C. MS (MALDI-TOF): $[M-H]^+$, *m/z* 1317.4. ^{1}H-NMR (400 MHz, DMSO-d_6, ppm): δ 7.80 (s, 3H), 7.73-7.69 (m, 14H), 7.53-7.52 (d, *J* = 8.4 Hz, 3H), 7.49-7.48 (d, *J* = 1.1 Hz, 3H), 7.24-7.22 (d, *J* = 8.4 Hz, 4H), 7.14 -7.12 (d, *J* = 8.7 Hz, 6H), 6.29 (s, 3H), 5.91 (s, 3H), 3.99-3.96 (t, *J* = 6.9 Hz, 6H), 2.02 (s, 9H), 1.77-1.70 (m, 6H), 1.49-1.43 (m, 6H), 0.95-0.91 (t, *J* = 7.3 Hz, 9H), ^{13}C-NMR (100 MHz, $CDCl_3$, ppm): δ 166.13, 150.28, 144.69, 144.53, 141.28, 137.87, 136.08, 135.55, 134.89, 127.73, 127.66, 127.50, 126.33, 126.12, 125.98, 125.04, 123.67, 122.08, 121.73, 115.73, 104.16, 81.36, 47.48, 29.17, 20.42, 18.61, 14.07. Anal. Calcd. for $C_{84}H_{75}N_3O_6S_3$: C, 76.51; H, 5.73; N, 3.19; S, 7.29. Found: C, 76.41; H, 5.61; N, 3.29; S, 7.21.

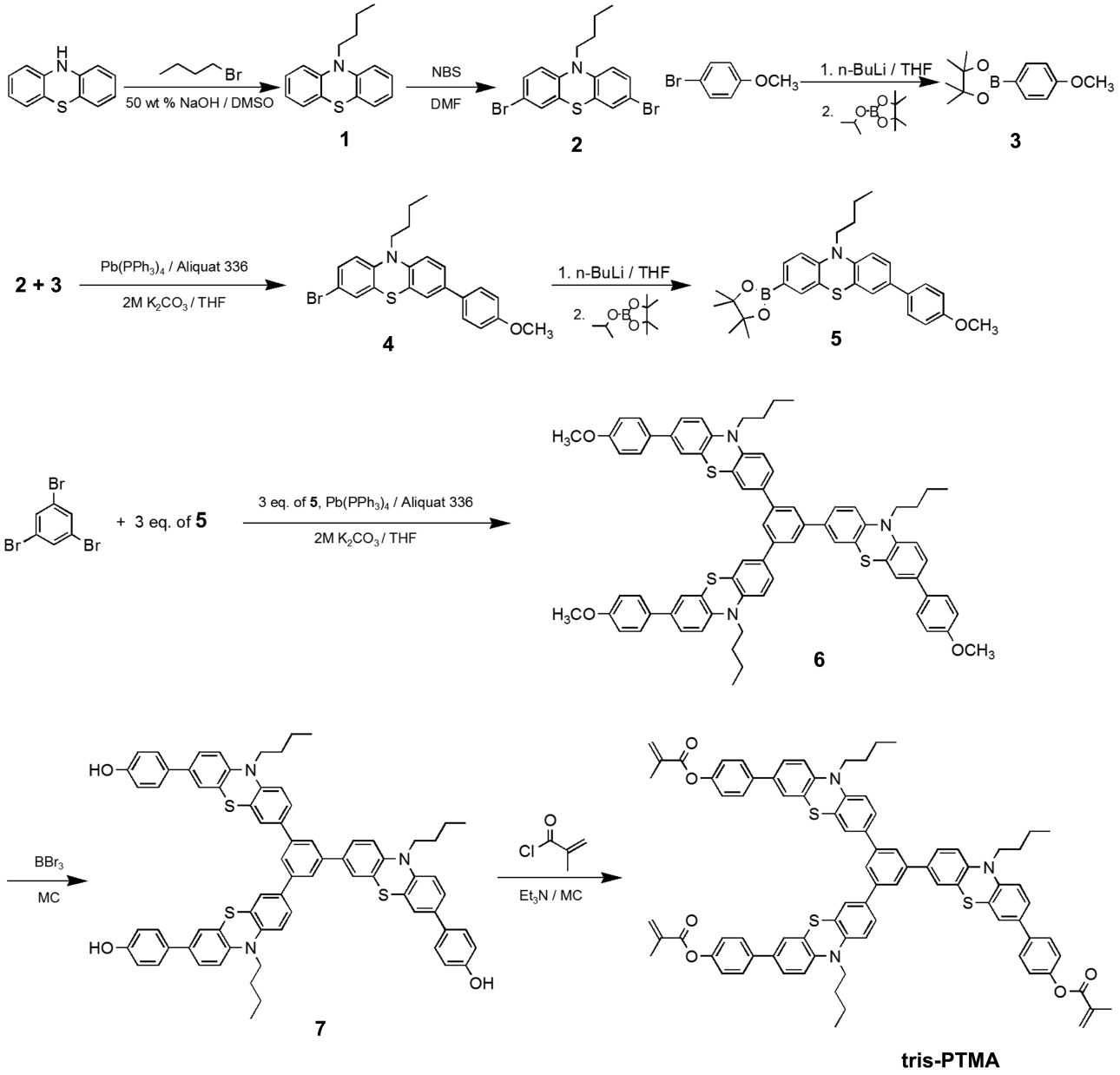
Device Fabrication. ITO-coated glass substrates were cleaned with deionized water, acetone, methanol, 2-propanol in ultrasonic bath. A solution of tris-PTMA layer (5 mg/mL in dichloroethane) was spin-coated onto the ITO. After spin coating, the thin film was heated up to 220 °C for 2 hours in the glove box. The typical thickness of film was 5-10 nm. The green emitting polymer (PF9B)[27] was dissolved in toluene and filtered through a 0.20-μm of PTFE syringe filter before spin coating. The typical thickness of emissive layer was 60 nm. A 1000 nm-thick Al was evaporated as cathode onto the surface of the emissive polymer (PF9B) film by thermal evaporation technique at 2.0×10^{-6} torr. The typical active area of the devices was 6 mm^2.

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. IR spectrum were obtained using a JASCO FT-IR spectrometer (JASCO FT/IR-4100). 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 nitrogen. The current density-voltage-brightness (*J*-V-B) characteristics were measured using a source meter (KEITHLEY 2400) and a luminometer (Minolta LS110).

Results and Discussion

Synthesis and Characterization of *in-situ* Thermally Curable Hyper-branched Phenothiazine. Scheme 1 shows the synthetic procedures for *in-situ* thermally curable hyper branched phenothiazine (tris-PTMA) with methyl methacryate, which is thermally curable unit. We introduce *n*-butyl substituent on phenithiazine to improve solubility. The yield of each synthetic step shows pretty high yield more than 62%. All the compounds were well characterized by elemental analysis, MASS, ^{1}H-NMR, and ^{13}C-NMR.

Figure 1 shows the TGA thermaogram of tris-PTMA, which is quite thermally stable up to 336 °C. The point of 5%-weight loss in TGA thermogram of tris-PTMA is 336 °C. In order to investigate thermal properties of tris-PTMA, we performed differential scanning calorimetry. As shown in Figure 2, tri-PTMA shows glass transition temperature (T_g)



Scheme 1. Synthesis of thermally curable tris-PTMA.

at 140 °C and broad endothermic process in the region of 141-190 °C with a peak at 170 °C in the first heating scan. In the second heating process, T_g appears at 158.7 °C, which is higher than T_g of the first scan. This is due to the network formation after curing. We cannot observe any endothermic process around 141-190 °C at second heating scan, indicating that thermally curing reaction is completed in the first heating scan. From the DSC thermogram one can easily notice that the endothermic process at 170 °C in the first scan is due to thermally curing reaction of methacrylate.

The chemical structures of before and after thermal curing of tri-PTMA were confirmed by the FT-IR spectrum. Thin film for FT-IR measurements was prepared by the drop casting of tris-PTMA solutions in chloroform (10 mg/mL) onto the pre-cleaned silicon wafer. Curing reaction of the film was performed at 220 °C for 2 hours. Thermally cured film at the temperature of less than 210 °C was completely or partially dissolved in organic solvent such as MC and chloroform. Figure 3 shows FT-IR spectrum of (a) before curing, (b) after curing, and (c) washed thermally cured tris-PTMA film. As shown in Figure 3(a), the absorption peaks at 1678 and 1037 cm^{-1} of tris-PTMA correspond to conjugated C=C stretching vibration and out-of-plane bending motion of C=C of methacrylate, respectively. In the FT-IR spectrum of cured tris-PTMA (Figure 3(b)), the absorption peaks at 1678 and 1037 cm^{-1} completely disappear after curing. In addition, the absorption intensity in FT-IR of cured tris-PTMA film washed with organic solvent (Figure 3(c)) such as MC, chloroform, and toluene is almost same as the cured tris-PTMA, indicating that thermally cured film is

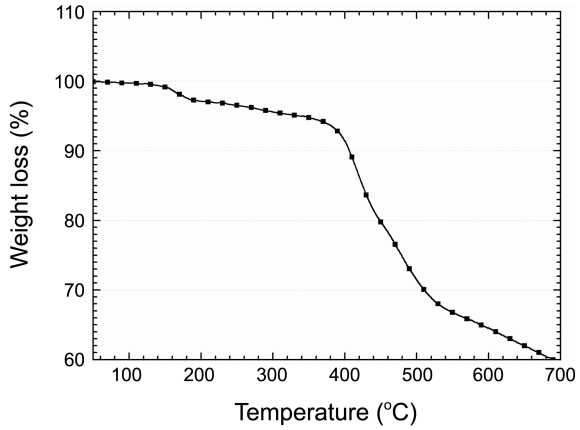


Figure 1. TGA thermorgram of tris-PTMA.

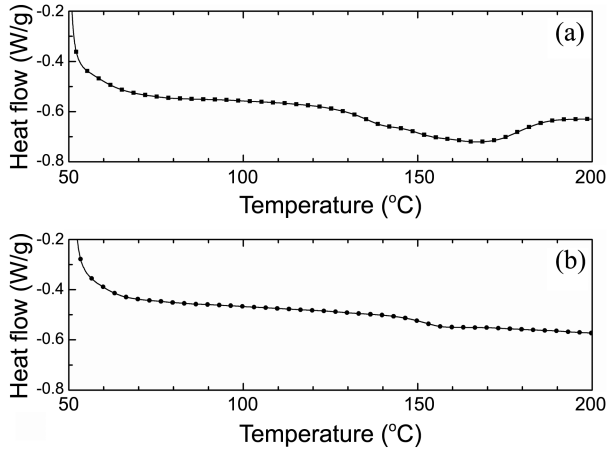


Figure 2. DSC thermorgram of tris-PTMA. ((a) first heating scan and (b) second heating scan).

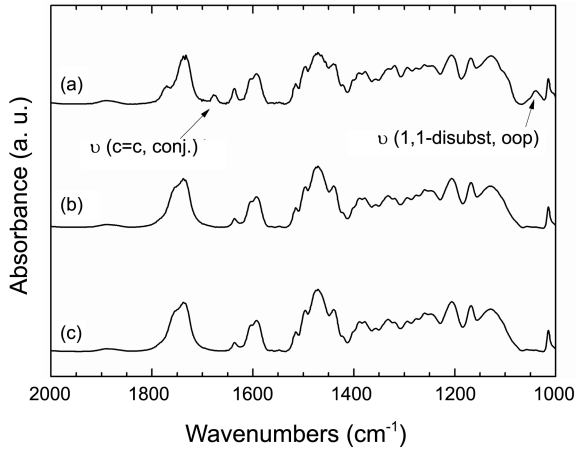


Figure 3. FT-IR spectrum of (a) before curing (b) after curing (c) washed cured tris-PTMA film.

very good solvent resistance. Figure 4 shows the UV-visible absorption spectrum of (a) tris-PTMA, (b) thermally cured tris-PTMA, and (c) washed thermally cured tris-PTMA film. The absorbance of thermally cured tris-PTMA (Figure 4(b)) is no big change after washing with organic solvents (Figure 4(c)). Also, the shape of UV-visible spectrum of cured films (Figure 4(b)) and washed cured film (Figure 4(c)) is almost

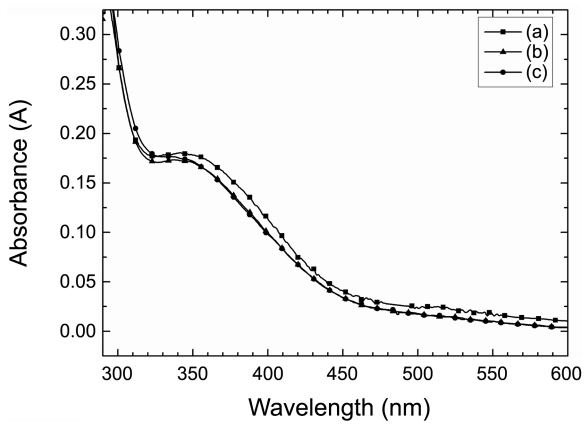


Figure 4. UV-Visible spectrum of (a) before curing (b) after curing (c) washed cured tris-PTMA film.

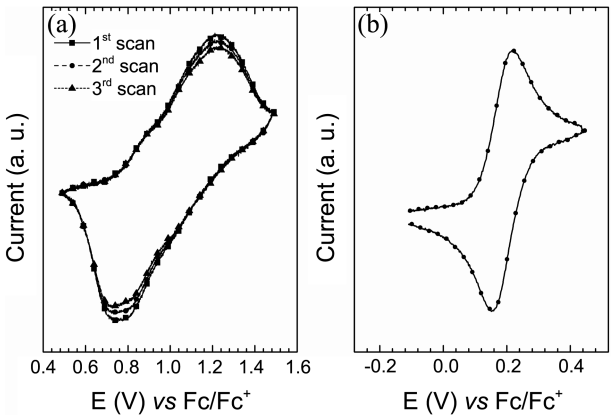


Figure 5. Cyclic voltammograms of (a) cured tris-PTMA film on ITO and (b) tris-PTMA solution in MC.

identical to that of pristine tris-PTMA film (Figure 4(a)).

Electrochemical and Electroluminescent Properties. Cyclic voltammetry (CV) is used to investigate the redox behavior of organic electronic materials and to access the energy levels. Figure 5 shows cyclic voltammogram of tris-PTMA film on ITO coated glass. Cyclic voltammograms of cured film shows quasi-reversible behavior and two oxidation peaks, which are 0.88 and 1.22 V *vs*. Fc/Fc^+. As shown in Figure 5(a), the magnitude of cathodic and anodic peak current of cured film on ITO does not change significantly upon three repeated redox scans in 0.1 M Bu_4NPF_6 in MC. This is indicating that cured tris-PTMA exhibits good electrochemical stability and solvent resistance. The HOMO energy level was estimated from the oxidation onset potential by the energy level of ferrocene is –4.8 eV. The HOMO energy level of cured tris-PTMA figured out from the oxidation onset potential of the first scan of the CV. The oxidation onset potential and HOMO energy level of *in-situ* thermally cured tris-PTMA are 0.74 V *vs*. Fc/Fc^+ and –5.54 eV, respectively. The HOMO energy level of cured tris-PTMA is much lower than the value of poly(hexylphenothiazine)[25,26] and thermally cured poly(alkylphenothiazine),[23] whose HOMO energy level are –4.9 ~ –5.0 eV. The oxidation onset potential and estimated HOMO energy level of tris-

Table 1. Optical, electrochemical, and thermal properties of tris-PTMA

	UV_{max} (nm)	E_{gap} (eV)	$E_{ox,peak}$ (V)	E_{onset} (V), HOMO (eV)[a]	T_d (°C)[b]	T_g (°C)
Cured tris-PTMA	345	2.78	0.89, 1.21	0.74, −5.54	-	
tris-PTMA		-	0.21	0.11, −4.91	336	140[c] 158.7[d]

[a]estimated from the oxidation onset potential by the energy level of ferrocene is –4.8 eV. [b]the point of 5%-weight loss. [c]glass transition temperature in the first heating scan. [d]glass transition temperature in the second heating scan

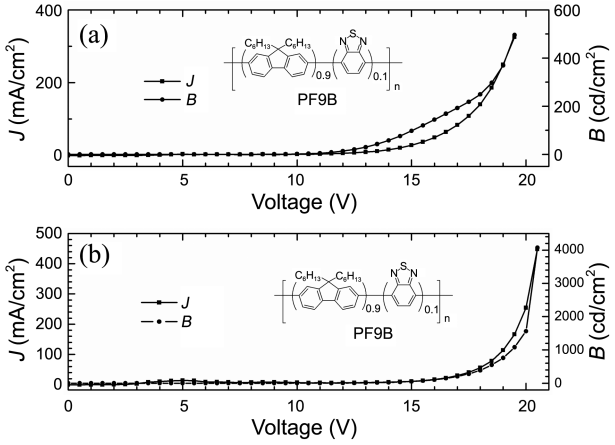


Figure 6. J-V-B curves of the device (a) ITO/PF9B/Al and (b) ITO/cured tris-PTMA/PF9B/Al.

PTMA solution in MC are 0.11 V *vs*. Fc/Fc^+ and −4.91 eV, respectively, which are almost same as the literature value. An oxidized electron from phenothiazine unit in the oxidation process would be trapped on high electron affinity carbonyl group in the methacrylate because the molecules are closely packed each other in the thermally cured film. This is because the HOMO energy level of cured film is dramatically lower than *ca*. –4.90 ~ −5.00 eV. The optical and electrochemical properties are summarized in Table 1.

In order to investigate hole injection and transporting properties of cured tris-PTMA, we fabricated double layer structured device, ITO/cured tris-PTMA/PF9B (60 nm)/Al. The thickness of films was measured by Alpha-Step IQ surface profiler. Figure 6 shows current density (*J*) and brightness (*B*) as a function of applied voltage (V) of the device. The turn-on voltage (defined as the voltage required to give a luminescent of 1 cd/m^2) of the device based on cured tris-PTMA was 10 V, which is same as the turn-on voltage of the device without tris-PTMA. However, the maximum luminance efficiency and brightness are 0.909 cd/A and 4071 cd/m^2, which are dramatically improved than the device without cured tris-PTMA (0.348 cd/A, 496 cd/m^2). From the electroluminescent properties, cured tris-PTMA is not act as hole injection layer but transporting layer. The recombination zone in the emissive layer is shifted away from the anode.

Conclusions

We synthesized a new *in-situ* thermally curable hyper-branched 10-butylphenothiazine with methacrylate as the thermally curable unit. From the UV-Visible and FT-IR spectroscopy, *in-situ* thermally cured tris-PTMA is safe to the successive layer coating by the solution process. Also, we confirm that the cured tris-PTMA is electrochemically stable. Double layer structured PLEDs based on cured tris-PTMA was fabricated successfully and the efficiency and maximum brightness of double layer structured devices exhibited better performances than those of the device without tris-PTMA. From the results, thermally cured tris-PTMA has good solvent resistance and hole injection/transporting properties.

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