Articles

Synthesis and Electro-optical Properties of π-Conjugated Polymer Based on 10-Hexylphenothiazine and Aromatic 1,2,4-Triazole

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New π-conjugated polymer with vinylene linkage, poly((10-hexyl-3,7-phenothiazine)-*alt*-(4-(4-butyl-phenyl)-3,5-diphenyl-4*H*-[1,2,4]triazole)-3,5-vinylene) (PTV-TAZ) was synthesized by the Heck coupling reaction. The photoluminescence (PL) maximum wavelength and the band gap energy of PTV-TAZ film were 555 nm and 2.41 eV, respectively. The HOMO energy level of PTV-TAZ was -4.99 eV, which was slightly lower than that of PTV (-4.89 eV). Electron deficient aromatic 1,2,4-triazole (TAZ) in the polymer backbone does not affect the HOMO energy level significantly. The maximum efficiency and brightness of double layer structured electroluminescent (EL) device (ITO/PEDOT (30 nm)/PTV-TAZ (60 nm)/Al) were 0.247 cd/A and 553 cd/m², respectively, which were significantly higher than those of the device based PTV (1.65×10^{-4} cd/A and 4.3 cd/m²). This is due to that TAZ unit improves electron transporting ability in the emissive layer. The turn-on voltage (defined as the voltage required to give a luminescence of 1 cd/m²) of brightness of the device based on PTV-TAZ was 12.0 V, which was similar to that the based on PTV (11.5 V). This is due to that the ionization potential of PTV-TAZ is very similar to that of PTV.

Key Words: Light-emitting polymer, Phenothiazine, 1,2,4-Triazole

Introduction

π-Conjugated polymers have been extensively studied for the last few decades in optoelectronics such as light-emitting diodes (LEDs),[1,2] photovoltaics (PVs),[3,4] thin film transistors (TFTs),[5-7] and electrochromic devices (ECDs).[8-10] Among these areas, tremendous efforts have already been made to improve the efficiency and color tuning of LEDs based on π-conjugated polymers. Synthesis of novel π-conjugated polymers is essential to improve the optoelectronic properties and stability. PPV derivatives with linear or branched alkoxy group (ROPPV) have good hole injection/transporting properties because of their high-lying HOMO energy level (-4.9 ~ -5.2 eV) *vs.* vacuum level. Therefore, one of the approaches to improve the performances of PPV derivatives is synthesis of new polymers with desired LUMO energy levels to enhance electron injection/transporting properties. PPV derivatives containing electron withdrawing unit such as the cyano (CN) group,[11,12] conjugated 1,3,4-oxadiazole,[13-15,16] and 1,2,4-triazole[17-20] in the main or side chain have been continuously reported. In these researches, although the electron injection/transporting properties were improved, the hole injection/transporting properties were suppressed compared to that of ROPPV. Other approaches to improve electron injection/transporting properties without affecting hole injection/transporting properties are to synthesize the polymers with electron withdrawing group, which is separated from the main chain *via* long alkyl chain.[20-23] Phenothiazine is potential building block for hole injection material and has high HOMO energy level because it has electron rich sulfur atom.[8,18,25-28] In addition, the

HOMO energy level of phenothiazine copolymer is dominated by contribution of phenothiazine unit.[29] Therefore, phenothiazine ring to be an excellent building block for improving hole injection ability of π-conjugated copolymers. However, the device based on poly(10-alkylphenothiazine) (PAT) are not enough to make efficient device since PAT has unbalanced charge injection/transporting property.

In this paper, we synthesized poly((10-hexyl-3,7-phenothiazine)-*alt*-(4-(4-butyl-phenyl)-3,5-diphenyl-4*H*-[1,2,4]triazole)-3,5-vinylene) (PTV-TAZ). In order to improve transporting property of the copolymer, we introduce 1,2,4-triazole unit (TAZ) in the polymer backbone. Phenothiazine and TAZ have highly non planar geometry so that interchain π-stacking of polymers would be reduced.[20,29-31] From the polymer structure, we can expect that PTV-TAZ would be very efficient polymer for LED. In order to compare opto-electrical and electroluminescent properties, we also synthesized poly(10-hexylphenothiazine-3,7-diyl) (PTV). We investigated the fundamental photophysical, electrochemical, and electroluminescent properties of the polymers.

Experimental

Materials and synthesis. Tetrahydrofuran (THF) was purified by distillation with sodium/benzophenone under nitrogen atmosphere before use. All chemicals were purchased from Aldrich Chemical Co. or Tokyo Chemical Industry (TCI) Chemical and used without any purification.

Synthesis of 10-hexyl-10*H*-phenothiazine (1): Benzyltriethylammonium chloride (30 mg) and 40 mL of 50% NaOH

were added to a solution of 10.0 g (50.0 mmol) of 10*H*-pheno-thiazine in 30 mL of DMSO. The reaction mixture was stirred for 30 min. A portion of 9.94 g (60.0 mmol) of *n*-hexylbromide was added to the reaction mixture then stirred for 24 hours at room temperature. The reaction mixture was neutralized with 2 M HCl and extracted with 100 mL of *n*-hexane three times. The combined organic layer was washed with aqueous brine and dried over anhydrous magnesium sulfate and evaporating the solvent using a rotary evaporator. The crude liquid product was purified by flash column chromatography using *n*-hexane to give colorless liquid (9.49 g, 67.0%). MS: [M^+], *m/z* 283. ^{1}H-NMR (400 MHz, CDCl$_3$, ppm): δ 7.12 (m, 4H), 6.96 (m, 2H), 1.64 (m, 2H), 1.35 (m, 2H), 1.21 (m, 4H), 0.80 (t, 3H). ^{13}C-NMR (100 MHz, CDCl$_3$, ppm): δ 145.19, 127.33, 127.10, 124.84, 122.27, 115.37, 47.40, 31.43, 26.81, 26.59, 22.55, 13.97. FTIR (cm^{-1}): *v* 3005, 2989, 2955, 2925, 1456, 1275, 1260. Anal. Calcd. for C$_{18}$H$_{21}$NS: C, 76.28; H, 7.47; N, 4.94; S, 11.31. Found: C, 76.18; H, 7.37; N, 4.84; S, 11.25.

10-Hexyl-10*H*-phenothiazine-3,7-dicarbaldehyde (2): A portion of 26.98 g (0.176 mol) of POCl$_3$ was slowly added into 12.86 g of *N,N*-dimethylformamide (DMF) at 4 °C. The reaction mixture was stirred for an hour at this temperature. This reaction mixture was slowly added into a solution of 5.00 g (17.6 mmol) of **1** in 80 mL of 1,2-dichloroethane at 4 °C. After complete addition of DMF and POCl$_3$ mixture, the reaction mixture was stirred at 90 °C for 24 hours. After cooling to room temperature, the reaction mixture was neutralized with aqueous K$_2$CO$_3$ and extracted with 100 mL of methylene chloride (MC) three times. The combined organic layer was washed with 300 mL of water and dried over anhydrous magnesium sulfate and evaporating the organic solvent using a rotary evaporator. The crude product was purified by flash column chromatography using *n*-hexane/methylene chloride (8/2). The light yellow oily product yield was 4.52 g (75.5%). MS: [M^+], *m/z* 339. ^{1}H-NMR (400 MHz, CDCl$_3$, ppm): δ 9.79 (d, 2H), 7.74 (d, 2H), 7.63 (d, 2H), 7.24 (d, 2H), 4.00 (t, 2H), 1.69 (m, 2H), 1.39 (m, 2H), 1.25 (m, 2H), 0.82 (t, 3H). ^{13}C-NMR (100 MHz, CDCl$_3$, ppm): δ 189.56, 148.55, 131.71, 130.06, 127.95, 124.02, 48.28, 31.08, 26.35, 26.16, 22.33, 13.76. FTIR (cm^{-1}): *v* 3005, 2979, 2933, 2875, 2830, 2741, 2628, 1741, 1599, 1464, 1238, 1200. Anal. Calcd. for C$_{20}$H$_{21}$NO$_2$S: C, 70.77; H, 6.24; N, 4.13; S, 9.45. Found: C, 71.02; H, 6.31; N, 4.05; S, 9.51.

10-Hexyl-3,7-divinyl-10*H*-phenothiazine (3): A portion of 8.40 mL of *n*-BuLi (21.0 mmol, 2.5 M solution in *n*-hexane) was slowly added to a suspension of 7.89 g (22.1 mmol) of methyl triphenylphosphonium bromide in 50 mL of anhydrous THF at -70 °C. After the completion of *n*-BuLi addition, the reaction mixture was stirred for 30 minutes at room temperature. The solution of 3.00 g (8.84 mmol) of **2** in 20 mL of anhydrous THF was added to above reaction mixture. The reaction mixture was gently refluxed for 4 hours. After cooling to room temperature, a portion of 100 mL of water and extracted with 100 mL of diethyl ether three times. The combined organic layer was washed with brine and followed by drying over anhydrous magnesium sulfate and evaporating the solvent in a rotary evaporator. The crude solid was purified by flash column chromatography using *n*-hexane/ethyl acetate (EA) (8/2). The light yellow oily product yield was 2.07 g (69.7 %). MS: [M^+],

m/z 335. ^{1}H-NMR (400 MHz, CDCl$_3$, ppm): δ 7.26 (m, 4H), 6.96 (d, 2H), 6.6 (t, 2H), 5.7 (d, 2H), 5.14 (d, 2H), 3.85 (t, 2H), 1.66 (m, 2H), 1.47 (m, 2H), 1.24 (m, 4H), 0.82 (m, 3H), 5.7 (t, 2H). ^{13}C-NMR (100 MHz, CDCl$_3$, ppm): δ 144.42, 135.50, 132.14, 132.04, 125.42, 124.81, 115.06, 112.15, 47.58, 31.42, 26.76, 26.58, 22.57, 13.97. FTIR (cm^{-1}): *v* 3084, 3070, 3003, 2965, 2925, 2854, 1625, 1473, 1418. Anal. Calcd. for C$_{22}$H$_{25}$NS: C, 78.76; H, 7.51; N, 4.17; S, 9.56. Found: C, 78.65; H, 7.45; N, 4.13; S, 9.50.

10-Hexyl-3,7-dibromo-10*H*-phenothiazine (4): A solution of 4.15 g (23.3 mmol) of *N*-bromosuccinimide (NBS) in 10 mL of DMF was added dropwise to a solution of 3.0 g (10.6 mmol) of compound **1** in 20 mL of DMF under argon atmosphere at 5 °C for a period of 30 min. After being stirred for 6 hours at room temperature, a portion of 100 mL of water was added into a reaction mixture then extracted with 100 mL of ethyl acetate three times. The combined organic layer was washed with aqueous sodium bisulfite (10 wt.%) and then dried over anhydrous MgSO$_4$. The solvent was removed by evaporation under reduced pressure. The crude product was purified by column chromatography on silica gel using *n*-hexane/MC (7/3). The yield of light yellow soild was 83.5% (4.1 g). MS [M^+]. *m/z* 441. mp: 50 - 53 °C. ^{1}H-NMR (400 MHz, CDCl$_3$, ppm): δ 7.35 (t, 4H), 6.94 (d, 2H), 3.8 (t, 2H), 1.6 (m, 2H), 1.33 (t, 2H), 1.22 (m, 4H), 0.81 (m, 3H). ^{13}C-NMR (100 MHz, CDCl$_3$, ppm): δ 143.94, 129.97, 129.52, 126.24, 116.50, 114.60, 47.47, 31.29, 26.50, 26.41, 22.50, 13.94. FTIR (cm^{-1}): *v* 3057, 2954, 2947, 2918, 1454, 1250, 1238, 874, 794. Anal. Calcd. for C$_{18}$H$_{19}$Br$_2$NS: C, 49.00; H, 4.34; N, 3.17; S, 7.27. Found: C, 49.10; H, 4.26; N, 3.13; S, 7.13.

4-Bromo-benzoic acid *N'*-(4-bromobenzoyl)-hydrazide (5): A solution of 4-bromobenzoyl chloride 4.91 of (22.3 mmol) in 10 mL of DMF was added into a solution of 4.80 g (22.3 mol) 4-bromobenzoic hydrazide and 2.26 g (22.3 mol) of triethyl-amine in 10 mL of DMF. The reaction mixture was stirred for 6 hours at room temperature. A portion of 100 mL of methanol was added to the reaction mixture and the precipitate was filtered and washed with 100 mL of methanol and 100 mL of water. The crude product purified by recrystallization from methanol. The white solid product yield was 73.8% (6.55 g). mp was not found up to 300 °C. MS: [M^+], *m/z* 398. ^{1}H-NMR (400 MHz, DMSO-*d$_6$*, ppm): δ 10.55 (br, 2H), 7.89-7.84 (m, 4H), 7.74-7.71 (d, *J* = 8.5 Hz, 2H), 7.54-7.52 (d, *J* = 8.5 Hz, 2H), 1.32 (s, 9H). ^{13}C-NMR (75 MHz, DMSO-*d$_6$*, ppm): δ 165.98, 165.50, 155.39, 132.34, 130.95, 130.34, 128.08, 126.13, 35.55, 31.79. FTIR (cm^{-1}): *v* 3191, 3055, 3024, 1590, 1556, 1496, 1261, 844, 834, 738. Anal. Calcd. for C$_{14}$H$_{10}$Br$_2$N$_2$O$_2$: C, 42.24; H, 2.53; N, 7.04. Found: C, 42.25; H, 2.49; N, 6.95.

3,5-Bis-(4-bromo-phenyl)-4-(4-butyl-phenyl)-4*H*-[1,2,4] triazole (6): A portion of 2.06 g (15.0 mmol) of PCl$_3$ was added to a solution of 8.95 g (60.0 mmol) of 4-butylaniline in 10 mL of 1,2-dichlorobenzene. The mixture was stirred at 100 °C for 1 hours then 3.98 g (10.0 mmol) of **4** was added to the reaction mixture. The reaction mixture was stirred at 190-200 °C for 24 hours and then cooled down to room temperature and 100 mL of 2 N HCl was added into the reaction mixture. The reaction mixture was filtered through Celite and washed with 200 mL of methylene chloride (MC). The filtrate was

washed with water then dried by anhydrous magnesium sulfate. The MC was removed using a rotary evaporator then 1,2-dichlrobenzene was removed by vacuum distillation. The crude solid product was purified by column chromatography using ethylacetate (EA)/MC (1:9 by volume). The product yield was 3.30 g (64.0%). MS: $[M^+]$, m/z 287. mp: 168 °C. ^{1}H-NMR (400 MHz, CDCl$_3$, ppm): δ 7.65 (s, 1H), 7.55-7.46 (m, 4H), 7.39-7.25 (m, 5H), 7.20-7.06 (m, 3H), 1.30 (s, 9H). ^{13}C-NMR (75 MHz, CDCl$_3$, ppm): δ 155.42, 153.68, 153.42, 135.47, 132.95, 132.13, 130.53, 130.29, 130.22, 129.38, 128.92, 128.23, 127.46, 125.84, 124.12, 122.85, 35.16, 31.52. FTIR (cm^{-1}): ν 3067, 2964, 2924, 2855, 1512, 1456, 1428, 1067, 1006. Anal. Calcd. for C$_{24}$H$_{22}$BrN$_3$: C, 66.67; H, 5.13; N, 9.72. Found: C, 66.86; H, 5.17; N, 9.70.

Poly(10-hexylphenothiazine-3,7-vinylene) (PTV): A portion of 0.1095 g (0.326 mmol) of **3**, 0.1441 g (0.326 mmol) of **4**, 0.0198 g (0.065 mmol) of tri-*o*-tolylphosphine, 0.202 mL (0.848 mmol) of tributylamine and 10 mg of Pd(OAc)$_2$ in degassed 5 mL of DMF stirred at 140 °C for 24 hours under argon atmosphere. The hot reaction mixture was poured into 300 mL of methanol, and then the polymer precipitate was collected by filtration. The filtered polymer precipitate was redissolved in 100 mL of chloroform and washed with 400 mL of deionized water several times. The polymer solution was dried over magnesium sulfate and the solvent was removed in a rotary evaporator. The polymer was dissolved in small amount of methylene chloride and the solution was poured into 300 mL of methanol. The polymer was collected by filtration. ^{1}H-NMR (400 MHz, CDCl$_3$, ppm): δ 7.24-7.18 (br, Ar-*H*), 6.8-6.76 (br, vinyl-*H*), 3.81-3.77 (br, N-*CH$_2$*), 1.78-1.73 (br, N-*CH$_2$CH$_2$*), 1.41-1.40 (br, -*CH$_2$*-), 1.29-1.24 (br, -*CH$_2$*-), 0.86-0.85 (br, -*CH$_3$*). FTIR (cm^{-1}): ν 3005, 2989, 2953, 2923, 2853, 1459, 1275, 1260, 954, 763, 750. Anal. Calcd. for C$_{21}$H$_{25}$NS: C, 77.97; H, 7.79; N, 4.33; S, 9.91. Found: C, 76.81; H, 6.59; N, 4.11; S, 8.71.

Poly((10-hexyl-3,7-phenothiazine)-*alt*-(4-(4-butyl-phenyl)-3,5-diphenyl-4*H*-1,2,4]triazole)-3,5-vinylene) (PTV-TAZ): PTV-TAZ was synthesized by the Heck coupling reaction between **3** and **6** in *N,N'*-dimethylformamide (DMF). Similar conditions were used as in the polymerization of **PTV**. ^{1}H-NMR (400 MHz, CDCl$_3$, ppm): δ 7.45-7.22 (br, Ar-*H*), 6.99-6.77 (br, vinyl-*H*), 3.78 (br, N-*CH$_2$*), 2.7 (br, -*CH$_2$*-), 2.3 (br, -*CH$_2$*-), 1.7 (br, -*CH$_2$*-), 1.6 (br, -*CH$_2$*-), 1.37-1.25 (br, -*CH$_2$*-), 0.95-0.87 (br, -*CH$_3$*). FTIR (cm^{-1}): ν 3005, 2989, 2954, 2926, 2856, 1609, 1458, 1275, 1260, 957, 763, 949. Anal. Calcd. for C$_{46}$H$_{52}$N$_4$S: C, 79.73; H, 7.56; N, 8.08; S, 4.63. Found: C, 80.56; H, 8.32; N, 5.23; S, 10.22.

EL device fabrication and characterization. ITO-coated glass substrates were cleaned with deionized water, acetone, methanol, 2-propanol in ultrasonic bath. A PEDOT (Baytron$^{(R)}$ P VP AI 4083) layer was spin-coated as hole injection layer (HIL) onto the ITO and dried at 140 °C for 10 minutes under the nitrogen. Before spin-coating, PEDOT was filtered through 0.45-μm of nylon syringe filter. The typical thickness of PEDOT and emissive layer were 30 and 60 nm, respectively. The emissive polymers were dissolved in chloroform and filtered through a 0.2-μm of PTFE syringe filter before spin coating. Al electrode was prepared onto the surface of the

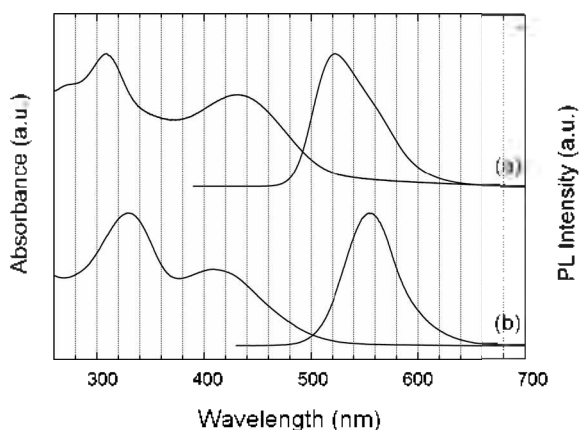emissive polymer film by thermal evaporation technique at ~ 10^{-5} torr. The typical active area of the devices was 4 mm^2.

Measurements. Synthesized compounds were characterized by ^{1}H-NMR and ^{13}C-NMR spectra, which were obtained with a JEOL JNM ECP-400 spectrometer. The elemental and MASS analysis of synthesized compounds were carried out on a Elementar Vario macro/micro elemental analyzer and Shimadzu GC-MS QP-5050A spectrometer. Thermogravimetric analysis (TGA) of the polymers was carried out under nitrogen atmosphere at a heating rate of 20 °C/min with a Perkin-Elmer TGA 7 thermal analyzer. UV-Visible (UV-Vis) and photoluminescence (PL) spectra of the polymers were recorded using a CARY100 CONC spectrophotometer and a HITACHI F-4500, respectively. Cyclic voltammetry was performed by a EG&G 362 Scanning Potentiostat with a three electrode cell in a solution of Bu$_4$NPF$_6$ (0.1 M) in freshly distilled MC at a scan rate of 100 mV/s. Pt wire was used as the counter and working electrode and an Ag/Ag$^+$ electrode was used as the reference electrode. Prior to each measurement, the cell was deoxygenated with argon. The EL spectra were recorded with a CCD array detector (Ocean Optics, USB 4000). And the current density-applied voltage-brightness (J-V-B) characteristics were measured using a source meter (KEITHLEY 2400) and a luminometer (Minolta LS110).

Results and Discussion

Synthetic procedures for monomers and polymers are shown
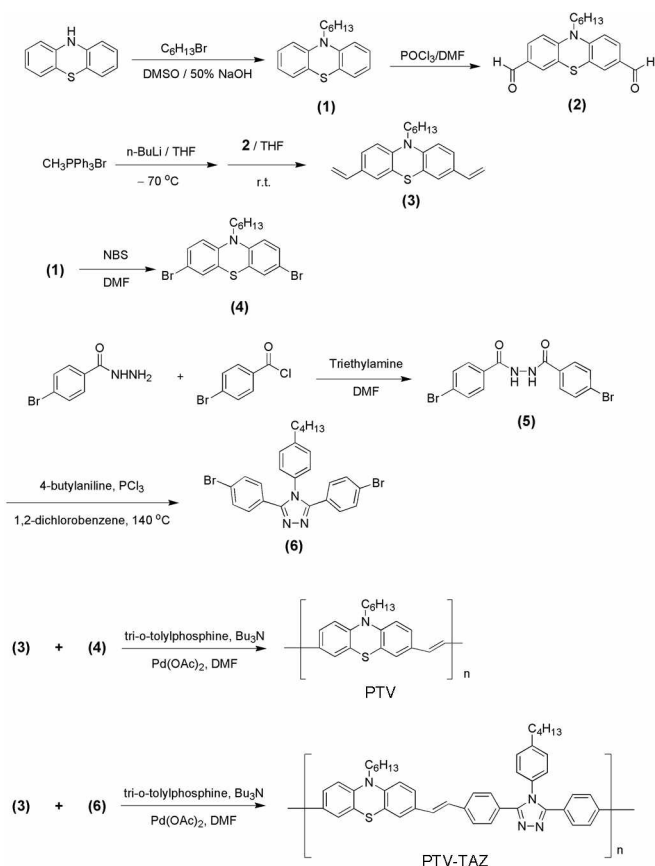
**Scheme 1.** Synthesis of monomers and polymers.

Figure 1. UV-Vis and PL spectrum of (a) PTV and (b) PTV-TAZ film.

Figure 2. Cyclic voltammograms (CVs) of (a) PTV and PTV-TAZ. CVs were performed in polymer solution in 0.1 M Bu₄NPF₆ solution in MC at a scan rate of 100 mV/s.

in Scheme 1. The Key monomer **6** prepared according to the literature procedures.[20] In this paper, synthetic procedures are described more detailed. In order to enhance the solubility of the polymer. we introduce *n*-butyl substituent in TAZ. All the compounds were well characterized by EA, MASS, ^{1}H-NMR, and ^{13}C-NMR. We also synthesize PTV to compare the electro-optical properties and EL performances with PTV-TAZ. The decomposition temperature and molecular weight of the polymers were summarized in Table 1. PTV and PTV-TAZ were readily soluble in chloroform, toluene, chlorobenzene and formed optically transparent film on ITO-coated glass or quartz plate.

Figure 1 shows UV-Vis and PL spectrum of polymer film. The PL maximum wavelength of PTV-TAZ film was 555 nm, which was 33 nm red-shifted compared to that of PTV film. This indicates that TAZ moiety elongates the effective π-conjugation length. As shown in Figure 1, PTV-TAZ film shows two absorption maximum at 330 and 410 nm, which are attributed from the TAZ moiety and the π-π^* transition of the main chain, respectively. The position of absorption maximum of π-π^* transition of the main chain of PTV-TAZ shows unusual feature. The maximum wavelength of main chain of PTV shows at 430 nm, which is 20 nm blue-shifted than that of PTV-TAZ.

In order to investigate the redox behavior of the polymer and assess the HOMO and LUMO energy levels, we performed cyclic voltammetry (CV). The HOMO energy level of π-conjugated polymers were estimated from the oxidation onset potential. As shown in Figure 2, the oxidation behavior of polymers exhibit reversible process. PTV shows two oxidation peaks at 0.32 and 0.56 V vs. Fc/Fc⁻, respectively, which correspond to the formation of the radical cation and dication of phenothiazine building block.[8,10] The oxidation peak of PTV-
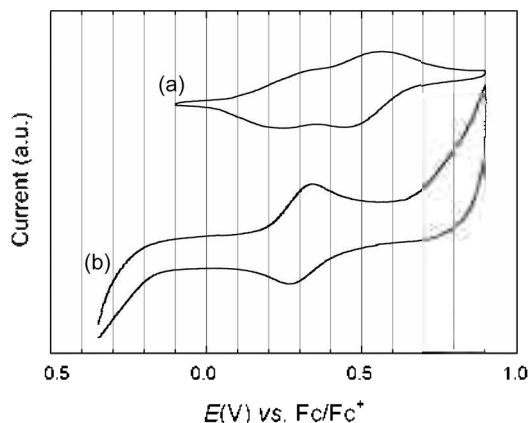
TAZ appeared at 0.34 V vs. Fc/Fc⁻, which is very similar to that of first oxidation peak of PTV and reversible process. The HOMO energy level estimated from the oxidation onset potential of PTV-TAZ is -4.99 eV, which is very close to that of PTV (-4.89 eV). Interestingly, TAZ building block does not affect the HOMO energy level significantly. This is presumably due to that the oxidation process in PTV-TAZ is dominated by phenothiazine unit and the delocalization of π-electrons in the phenothiazine based polymer is limited by the nonplanarity of phenothiazine unit. In addition, the nonplanarity of TAZ ring would be one of the reasons for exhibiting similar HOMO energy level. The LUMO energy level of polymers are estimated from the HOMO energy level and band gap energy because the reduction process of PTV and PTV-TAZ does not observed in the range from 0 to -3.0 V vs. Fc/Fc⁻. The LUMO energy level of PTV and PTV-TAZ figured out from the band gap and HOMO energy level are -2.46 and -2.58 eV, respectively. From the electrochemical data of polymers, phenothiazine is potential material for improving the hole injection ability from ITO or PEDOT to PTV-TAZ.

In order to investigate EL properties of the polymer, we fabricated the EL devices based on ITO/PEDOT (30 nm)/polymer (60 nm)/Al. As shown in Figure 3, the EL spectrum of the device based on PTV and PTV-TAZ are almost identical to those of PL spectrum. This indicates that the excited species in EL are very similar to PL. The current density and brightness plotted as a function of applied voltage of the devices are shown in Figure 4, showing that typical rectification characteristics. The turn-on voltages brightness (defined as the voltage required to give a luminescence of 1 cd/m²) of PTV-TAZ

Table 1. Summary of physical properties of the polymers.

	T_d (°C)[a]	T_g	M_n	M_w	UV$_{max,film}$ (nm)	PL$_{max, film}$ (nm)	HOMO (eV)[b]	E_{gap} (eV)[c]	LUMO (eV)[d]
PTV	274	123	8200	13400	308, 430	523	-4.89	2.41	-2.48
PTV-TAZ	298	141	11500	15400	330, 410	555	-4.99	2.41	-2.58

[a]Onset decomposition temperature was measured by TGA under nitrogen. [b]Estimated from the onset oxidation potential in the cyclic voltammogram. [c]Figured out from the absorption edge of the UV-Vis spectrum. [d]Estimated from the HOMO and E_{gap}.
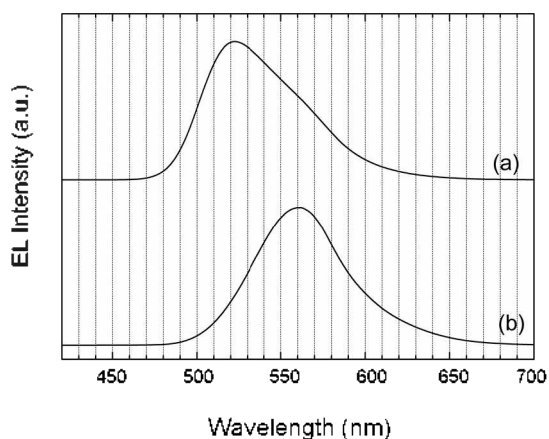
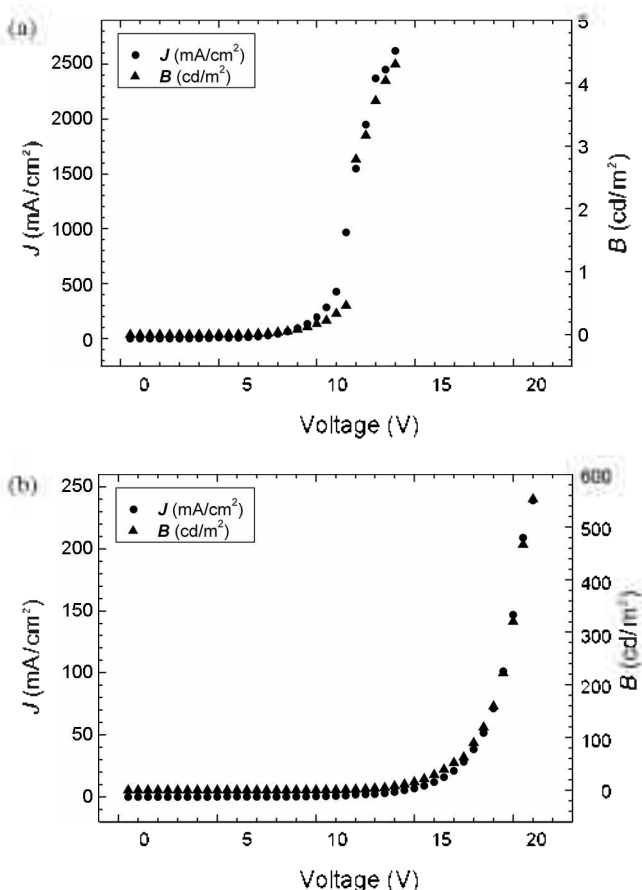**Figure 3.** EL spectrum of (a) PTV and (b) PTV-TAZ.

Figure 4. Current Density - Voltage - Brightness curves of (a) ITO/PEDOT/PTV/Al and (b) ITO/PEDOT/PTV-TAZ/Al.

based device is 12.0 V. which is slightly higher than those of the device based on PTV (11.5 V). This indicates that the hole injection efficiency from the anode to PTV-TAZ is very similar that of PTV. This result strongly supports the HOMO energy level data from the cyclic voltammetry. The maximum brightness and efficiency of the device based on PTV-TAZ (553 cd/m² and 0.247 cd/A) are significantly higher than those of PTV (4.3 cd/m² and 1.65 × 10⁴ cd/A) based device. Low performance of PTV based device is due to unbalanced charge

injection/transporting ability.[29] PTV is good *p*-type conductor and poor electron conductor. However. PTV-TAZ shows superior performances than PTV. This is presumably due to that PTV-TAZ has good electron transporting properties compared to PTV in spite of similar LUMO energy level.

Conclusions

We synthesized new π-conjugated alternating copolymer with vinylene linkage based on 10-hexylphenothiazine and TAZ through the well known palladium catalyzed Heck coupling reaction. The chemical structures of the polymers were characterized by ¹H-NMR spectroscopy. The HOMO energy level of PTV-TAZ figured out from the CV was very similar to that of polymer without TAZ. This indicates that the ionization potential of the polymer dominated by phenothiazine. The device efficiency based on PTV-TAZ was significantly higher than that of the device based on PTV. From the results, phenothiazine is excellent hole injection building block.

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