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Synthesis, Optical, and Electroluminescent Properties of Alternating Copolymer Based on Phenothiazine and Fluorene with Oxadiazole Pendant

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A new alternating copolymer based on phenothiazine-fluorene with aromatic 1,3,4-oxadiazole (OXD) as a side chain (poly(10-{4-[5-(4-tert-butyl-phenyl)-[1,3,4]oxadiazol-2-yl]-phenyl}-phenothiazine-3,7-diyl-alt-9,9-dihexyl-2,7-fluorene, PTOXDPF) was synthesized by the Suzuki coupling reaction. The maximum absorption wavelength of PTOXDPF solution showed at 410 nm which was dramatically blue-shifted than that of the polymer without OXD (poly(10-hexylphenothiazine-3,7-diyl-alt-9,9-dihexyl-2,7-fluorene, PTPF). This is due to that the presence of OXD pendant reduces the possibility of inter-chain interactions. The HOMO energy level of PTOXDPF estimated from the cyclic voltammetry was -5.13 eV, which was similar to the polymer without OXD pendant (PTPF). The OXD pendant does not affect HOMO energy level significantly. This is due to that oxidation potential of PTOXDPF dominated by the phenothiazine unit. The maximum efficiency and brightness of the electroluminescent (EL) device based on PTOXDPF (ITO/PEDOT/PTOXDPF/Al) were 45.4 cd/m² and 5.21 × 10⁻² cd/A, which were dramatically higher than PTPF (2.65 cd/m² and 1.32 × 10⁻³ cd/A). This is presumably due to that the OXD pendant in PTOXDPF improves the electron transporting ability in the emissive layer.

Keywords Light-emitting diode; Phenothiazine; Fluorene; 1; 3; 4-Oxadiazole

Introduction

Since the first report of the polymer light emitting diode (PLED) by Friend group [1]. Tremendous efforts have already been made to improve the efficiency of LEDs based on poly(*p*-phenylenevinylene) (PPV), polyfluorene (PF). One of the strategies to improve efficiency of PLED is to synthesis new efficient polymers with electron transporting materials. It has been continuously reported that the π -conjugated polymers containing 1,3,4-oxadiazole (OXD) [2–5] 1,2,4-triazole (TAZ) [6,7] in the main chain or side chain to improve device efficiency. Recently, luminescent properties of π -conjugated polymers based on 10-alkylphenothiazine have been reported [8–10]. Phenothiazine is very strong

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electron donor since it has sulfur atom so that the polymers based on phenothiazine are very good hole injection/transporting properties. However, EL devices based phenothiazine polymers have extremely low efficiency since hole injection and transporting properties are superior to electron injection and transporting properties.

In this paper, we attempt to improve EL efficiency of polymer based on phenothiazine by introducing OXD unit as a side chain, which has good electron transporting properties. We also synthesize Poly(10-hexylphenothiazine-3,7-diyl-alt-9,9-dihexyl-2,7-fluorene) (PTPF) to compare the optical, electrochemical and EL properties with a new poly(10-{4-[5-(4-tert-butyl-phenyl)-[1,3,4]oxadiazol-2-yl]-phenyl}-phenothiazine-3,7-diyl-alt-9,9-dihexyl-2,7-fluorene) (PTOXDPF), which has electron withdrawing OXD as a side chain.

Experimental

Materials

All chemicals were purchased from Aldrich Chemical Co. or Tokyo Chemical Industry (TCI) Chemical and used as received. 10-hexyl-3,7-dibromo-10*H*-phenothiazine [11–13] was synthesized according to the literature procedures.

Synthesis of 4-Phenothiazin-10-yl-benzonitrile (1). A portion of 1.99 g (82.8 mmol) of NaH in 80 mL of anhydrous *N,N*-dimethylformamide (DMF) was stirred for 30 min at 0°C. A portion of 15.0 g (75.3 mmol) of 10*H*-phenothiazine and 10.03 g (82.8 mmol) of 4-fluorobenzonitrile was slowly added into a slurry of NaH in DMF under N₂ atmosphere. After completion of addition of 10*H*-phenothiazine and 4-fluorobenzonitrile, the reaction mixture was stirred at 170°C for 15 hours. The reaction mixture cooling down to room temperature, 100 mL of water was added into the reaction mixture then extracted with 100 mL of MC three times. The combined organic layer was dried over anhydrous magnesium sulfate then the solvent was removed using a rotary evaporator under reduced pressure. The crude product was purified by flash chromatography using *n*-hexane:EA (4:1). The white solid product was 14.5 g (64.1%). MS [*M*⁺], *m/z* 300. mp: 159°C. ¹H-NMR (400 MHz, CDCl₃, ppm): δ 7.72 (d, 2H), 7.53 (d, 2H), 7.39 (t, 2H), 7.32 (d, 2H), 7.27 (t, 2H), 7.09 (d, 2H). ¹³C-NMR (100 MHz, CDCl₃, ppm): δ 148.99, 141.09, 133.64, 133.02, 128.93, 127.47, 126.27, 125.87, 119.48, 117.04, 104.33. Anal. Calcd. for C₁₉H₁₂N₂S: C, 75.97; H, 4.03; N, 9.33; S, 10.67. Found: C, 75.52; H, 4.14; N, 9.28; S, 10.76.

Synthesis of 4-Phenothiazin-10-yl-benzoic acid (2)

A portion of 10.0 g (33.2 mmol) of **1** and 26.6 g (47.4 mmol) of KOH was added into a 50 mL of ethanol:water(7:3). The reaction mixture was refluxed for 24 hours. The reaction mixture cooled down to room temperature then neutralized with 5% HCl. The reaction mixture poured to 1000 mL of water then the precipitate was filtered. The crude precipitate was purified by recrystallization from methanol. The white solid product yield was 8.12 g (76.3%). MS: [*M*⁺], *m/z* 319. mp: 224°C. ¹H-NMR (400 MHz, DMSO-*d*₆, ppm): δ 10.48 (s, 1H), 8.46 (d, 2H), 8.06 (dd, 2H), 7.70 (d, 2H), 7.51 (t, 2H), 7.33 (t, 2H), 6.73 (d, 2H). ¹³C-NMR (100 MHz, DMSO-*d*₆, ppm): δ 166.76, 146.72, 141.96, 131.53, 127.76, 127.58, 126.91, 126.29, 124.72, 122.54, 121.56. Anal. Calcd. for C₁₉H₁₃NO₂S: C, 71.45; H, 4.10; N, 4.39; S, 10.04. Found: C, 71.65; H, 4.15; N, 4.34; S, 10.24.

Synthesis of 4-tert-Butyl-benzoic acid N'-(4-phenothiazin-10-yl-benzoyl)-hydrazide (3). A mixture of 8.00 g (25.04 mmol) and **2**, 5.76 g (29.96 mmol) of 4-tert-butyl-benzoic hydrazide, and 5.76 g (30.08 mmol) of 1-ethyl-3-(3-di-methylaminopropyl)-carbodiimidehydrochloride (EDCI) in 30 mL of DMF was stirred for 5 hours at room temperature. A portion of 100 mL of water was added into the reaction mixture then the precipitate was filtered. The crude precipitate was purified by recrystallization from methanol. The white product yield was 10.0 g (80.9%). MS: $[M^+]$, m/z 493. mp: 313–315°C. $^1\text{H-NMR}$ (400 MHz, $\text{DMSO-}d_6$, ppm): δ 10.48 (s, 2H), 8.06 (d, 2H), 7.87 (d, 2H), 7.54 (d, 2H), 7.39 (d, 2H), 7.27 (d, 2H), 7.13 (t, 2H), 7.03 (t, 2H), 6.64 (d, 2H), 1.32 (s, 9H). $^{13}\text{C-NMR}$ (100 MHz, $\text{DMSO-}d_6$, ppm): δ 165.74, 165.14, 154.68, 145.06, 142.43, 129.93, 129.82, 127.49, 127.41, 127.31, 125.22, 124.11, 124.06, 122.91, 121.06, 119.79, 34.65, 30.88. Anal. Calcd. for $\text{C}_{30}\text{H}_{27}\text{N}_3\text{O}_2\text{S}$: C, 73.00; H, 5.51; N, 8.51; S, 6.50. Found: C, 73.20; H, 5.58; N, 8.42; S, 6.46.

Synthesis of 10-{4-[5-(4-tert-Butyl-phenyl)-[1,3,4]oxadiazol-2-yl]-phenyl}-10H-phenothiazine (4)

A portion of 4.00 g (8.12 mmol) of compound **3** in 10 mL of freshly distilled POCl_3 was refluxed for 12 hours then cooled to room temperature. The reaction mixture was slowly poured into crushed ice and the precipitate was filtered. The crude solid was dissolved in chloroform and wash with brine and aqueous NaOH. The organic layer was dried over anhydrous magnesium sulfate followed by evaporating the solvent in a rotary evaporator. The crude product was purified by flash chromatography using EA:MC (1:4). The yield of the yellow oily product was 2.92 g (76.0%). MS: $[M^+]$, m/z 475. $^1\text{H-NMR}$ (400 MHz, CDCl_3 , ppm): δ 8.20 (d, 2H), 8.05 (d, 2H), 7.66 (d, 2H), 7.44 (d, 2H), 7.34 (d, 2H), 7.21 (T, 2H), 7.10 (T, 2H), 6.86 (d, 2H), 1.34 (s, 9H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3 , ppm): δ 165.33, 163.20, 155.31, 146.18, 142.58, 128.78, 127.80, 127.07, 126.87, 126.70, 126.03, 124.38, 124.19, 122.91, 121.06, 120.32, 35.04, 31.08. Anal. Calcd. for $\text{C}_{30}\text{H}_{25}\text{N}_3\text{OS}$: C, 75.76; H, 5.30; N, 8.84; S, 6.74. Found: C, 75.30; H, 5.34; N, 8.90; S, 6.67.

Synthesis of 3,7-dibromo-10-{4-[5-(4-tert-butyl-phenyl)-[1,3,4]oxadiazol-2-yl]-phenyl}-10H-phenothiazine (5)

A solution of 2.34 g (13.1 mmol) of NBS in 10 mL of DMF was added dropwise to a solution of 2.5 g (5.26 mmol) of compound **4** in 30 mL of DMF under nitrogen 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 ethylacetate 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 EA/MC (1/4). The yield of light yellow solid was 0.58 g (17.4%). MS $[M^+]$, m/z 633. mp: 252–254°C. $^1\text{H-NMR}$ (400 MHz, CDCl_3 , ppm): δ 8.50 (d, 2H), 8.11 (m, 4H), 7.60 (m, 4H), 7.26 (d, 2H), 6.63 (d, 2H), 1.39 (s, 9H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3 , ppm): δ 165.33, 163.20, 155.89, 141.30, 137.09, 135.71, 133.93, 131.14, 129.97, 126.88, 126.19, 125.76, 124.12, 120.64, 118.94, 114.70, 35.13, 31.07. Anal. Calcd. for $\text{C}_{30}\text{H}_{23}\text{Br}_2\text{N}_3\text{OS}$: C, 56.89; H, 3.66; Br, 25.23; N, 6.63; S, 5.06. Found: C, 56.14; H, 3.63; N, 6.36; S, 5.11.

Polymerization of poly(10-{4-[5-(4-tert-butyl-phenyl)-[1,3,4]oxadiazol-2-yl]-phenyl}-phenothiazine-3,7-diyl-alt-9,9-dihexyl-2,7-fluorene) (PTOXDPF). A portion of

0.3167 g (0.5 mmol) of **5**, 0.2512 g (0.5 mmol) of 9,9-dihexylfluorene-2,7-bis(trimethyleneborate), tetrakis(triphenylphosphine) palladium ($\text{Pd}(\text{PPh}_3)_4$) (0.01 mmol), several drops of aliquat 336 were dissolved in a mixture of 3 mL of degassed toluene and 2 mL of degassed 2 M K_2CO_3 (aq). The mixture was stirred at 80°C for 2 days under argon atmosphere. At the end of polymerization, 0.1 mL of 1-bromo-4-tertbutylbenzene was added as a monofunctional end-capping reagent. After being stirred the mixture for 12 hours, 60 mg of phenyl boronic acid was added and stirred for 12 hours. After cooling to room temperature, the reaction mixture was poured into 250 mL of methanol. The precipitate was filtered and dissolved in 40 mL of chloroform, extracted with 100 mL of deionized water three times. The organic layer dried over anhydrous MgSO_4 and the solvent was removed by evaporation under reduced pressure. The polymer was dissolved small amount of methylene chloride and poured into a stirred methanol. The polymer was collected by filtration and dried under vacuum for 12 hours. $^1\text{H-NMR}$ (400MHz, CDCl_3 , ppm): δ 8.57–8.53 (br, Ar-H), 8.37–8.32 (br, Ar-H), 8.19–8.14 (br, Ar-H), 7.87–7.81 (br, Ar-H), 6.91–6.90 (br, Ar-H), 6.68–6.67 (br, Ar-H), 2.72–2.59 (br, $-\text{CH}_2-$), 2.09–2.05 (br, $-\text{CH}_2-$), 1.40–1.37 (br, $-\text{C}(\text{CH}_3)_4$), 1.24–1.09 (br, $-\text{CH}_2\text{CH}_2-$), 0.88–0.74 (br, $-\text{CH}_3$).

Polymerization of Poly(10-hexylphenothiazine-3,7-diyl-alt-9,9-dihexyl-2,7-fluorene) (PTPF)

PTPF was synthesized by the Suzuki coupling reaction between 2,7-dibromo-9H-hexyl-phenothiazine and 9,9-dihexylfluorene-2,7-bis(trimethyleneborate). Similar conditions were used as in the polymerization of **PTOXDPF**. $^1\text{H-NMR}$ (400MHz, CDCl_3 , ppm): δ 7.68–7.52 (br, Ar-H), 7.36–7.30 (br, Ar-H), 3.86–3.83 (br, N- CH_2), 2.31–1.99 (br, $-\text{CH}_2-$), 1.47–1.31 (br, $-\text{CH}_2-$), 1.20–1.07 (br, $-\text{CH}_2-$), 0.95–0.86 (br, $-\text{CH}_2-$), 0.71 (br, $-\text{CH}_3$).

Measurements. Synthesized compounds were characterized by $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra, which are 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 $20^\circ\text{C}/\text{min}$ 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_4NPF_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.

EL Device Fabrication and Characterization

ITO-coated glass substrates were cleaned with deionized water, acetone, methanol, 2-propanol in ultrasonic bath. A PEDOT:PSS (Baytron® P VP Al 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:PSS was filtered through 0.45- μm of nylon syringe filter. The emissive polymers were dissolved in chlorobenzene and filtered through a 0.2- μm of PTFE syringe filters before spin coating. The thickness of films was measured by Alpha-Step IQ surface profiler (KLA-Tencor Co.) Al electrode was prepared onto the surface of the emissive polymer film by thermal evaporation technique at $\sim 10^{-5}$ torr. The

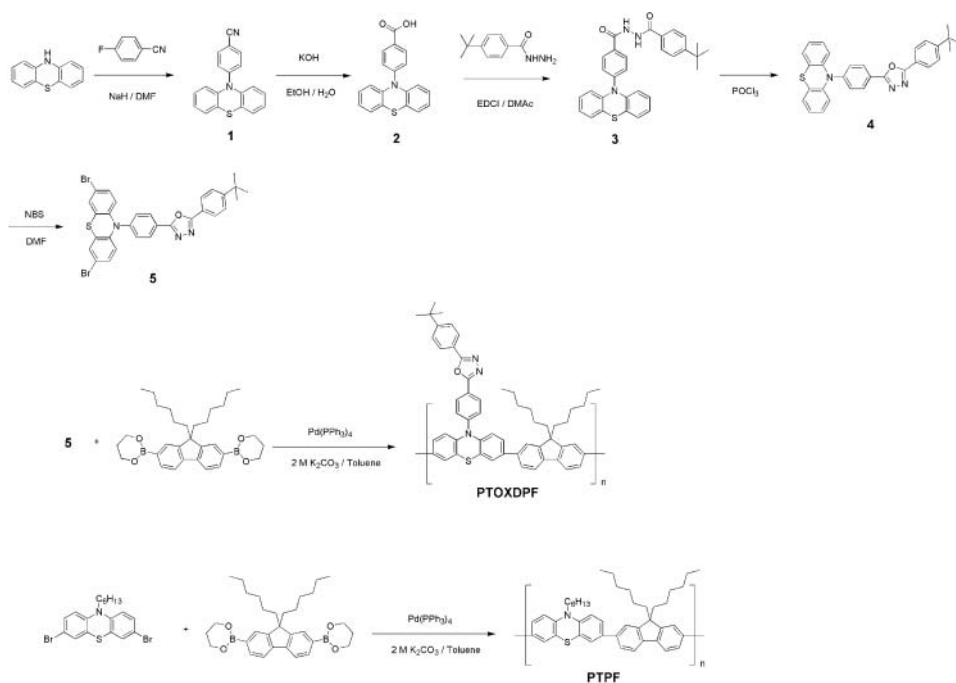
typical active area of the devices was 3.14 mm². The EL spectra were recorded with a CCD array detector (Ocean Optics, USB4000). And the current density-applied voltage-brightness (J-V-B) characteristics were measured using a source meter (KEITHLEY 2400) a luminometer (Minolta LS110).

Results and Discussion

Synthesis and Characterization

Scheme 1 shows the synthetic schemes for monomer and polymers, respectively. In order to improve the solubility of polymers, we introduce *tert*-butyl substituent in 1,3,4-oxadiazole. All the compounds were well characterized by ¹H-NMR, ¹³C-NMR, MASS, and EA. The polymerization reactions were conducted by the well known Suzuki coupling reaction. The preparation of PTPF and the monomers for PTPF were synthesized according to the literature procedures [8]. The chemical structure of PTOXDPF was confirmed by the ¹H-NMR.

Weight loss of 5% of PTOXDPF occurred at 310°C in the TGA thermogram. The glass transition temperature of PTOXDPF appeared at 175°C in the DSC thermogram, which is slightly higher than PTPF (165°C). The number-average molecular weight of PTOXDPF and PTPF measured by GPC were 6900 and 11500 with a polydispersity index of 1.92 and 2.31, respectively. PTOXDPF and PTPF were readily soluble in common organic solvents such as chloroform, chlorobenzene, dichlorobenzene, toluene and it is possible to prepare smooth and optically clear film by spin coating.



Scheme 1. Synthesis of monomer and polymer.

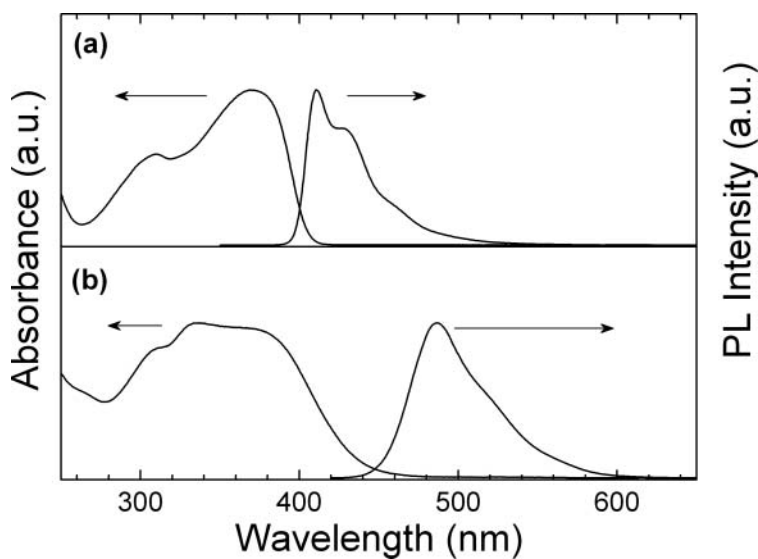


Figure 1. UV-Vis and PL spectrum of (a) PTOXDPF and (b) PTPF solution in chloroform.

Optical and Electrochemical Properties

Figure 1 shows UV-Vis and PL spectrum of polymer solutions in chloroform. The position and shape of PL spectrum of PTPF solution is almost same as the literature data [8]. However, the PL maximum wavelength of PTOXDPF appears at 410 nm, which is dramatically blue-shifted than that of PTPF (486 nm). As shown in Figure 2, Similar features were observed in the PL spectrum of polymer film. The PL maximum wavelength of PTOXDPF

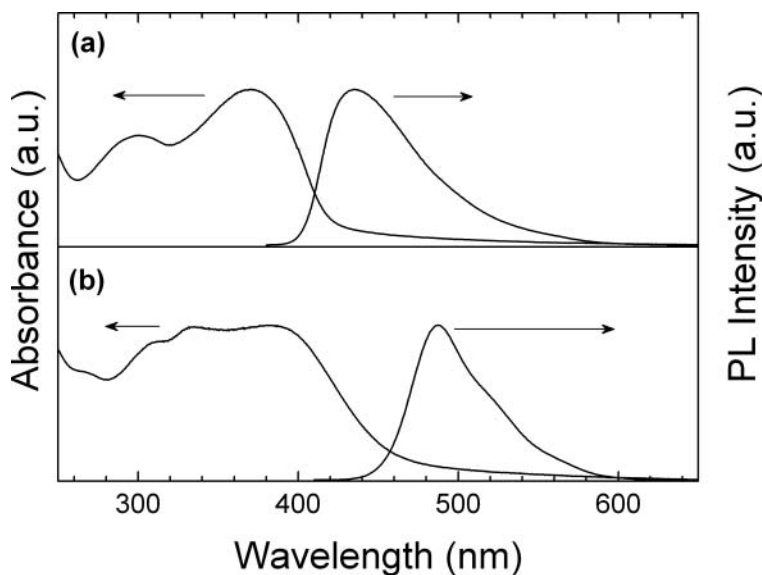


Figure 2. UV-Vis and PL spectrum of (a) PTOXDPF and (b) PTPF film.

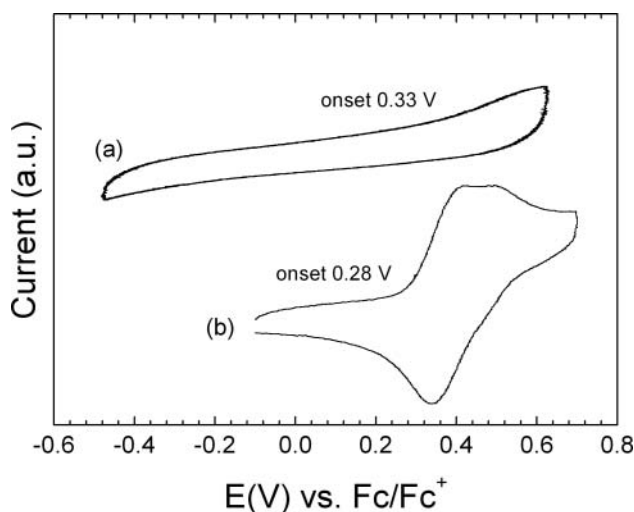


Figure 3. Cyclic voltammogram of PTOXDPF. CVs were performed in polymer solution in 0.1 M Bu_4NPF_6 solution in MC at a scan rate of 100 mV/s.

is observed at 435 nm, which is also blue-shifted than that of PTPF film (488 nm). This is presumably due to the bulky 1,3,4-oxadiazole (OXD) substituent on the 10-position of phenothiazine. The presence of OXD pendant reduces the possibility of inter-chain interactions. The absorption peak at 309 and 300 nm of PTOXDPF solution and film corresponds to the π - π^* transition of OXD pendant. The additional absorption peak at 370 nm of PTOXDPF solution and 370 nm of PTOXDPF film correspond to the π - π^* transition of main chain.

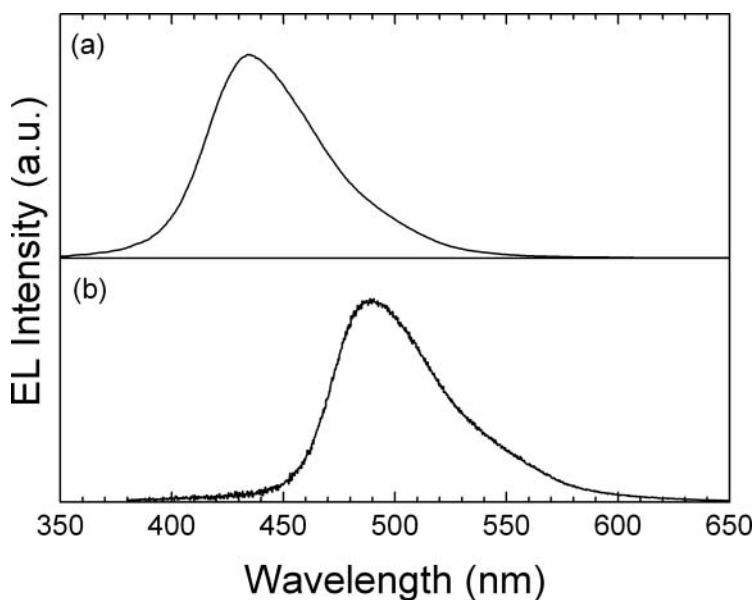


Figure 4. EL spectrum of (a) ITO/PEDOT/PTOXDPF/Al and (b) ITO/PEDOT/PTPF/Al.

The position and shape of UV-Visible spectrum of PTOXDPF film is very similar to that of PTOXDPF solution. This indicates that OXD pendants impede formation of inter-chain excimer or aggregate in the solid state [14]. The band gap energy of PTOXDPF and PTPF figured out from the absorption edge of UV-Vis spectrum are 2.97 and 2.74 eV, respectively.

The energy levels of light emitting polymer are important for understanding charge injection processes in EL devices. We performed cyclic voltammetry to estimate the energy levels [15,16] of polymer and to investigate redox behavior of the polymer. The potential of cyclic voltammogram was corrected by the oxidation onset potential of ferrocene/ferrocenium (Fc/Fc^+) vs. Ag/Ag^+ . As shown in Figure 3 (a), the oxidation behavior of PTOXDPF is irreversible process. However, oxidation behavior of PTPF (Figure 3 (b)) shows reversible process. The HOMO energy level estimated from the oxidation onset

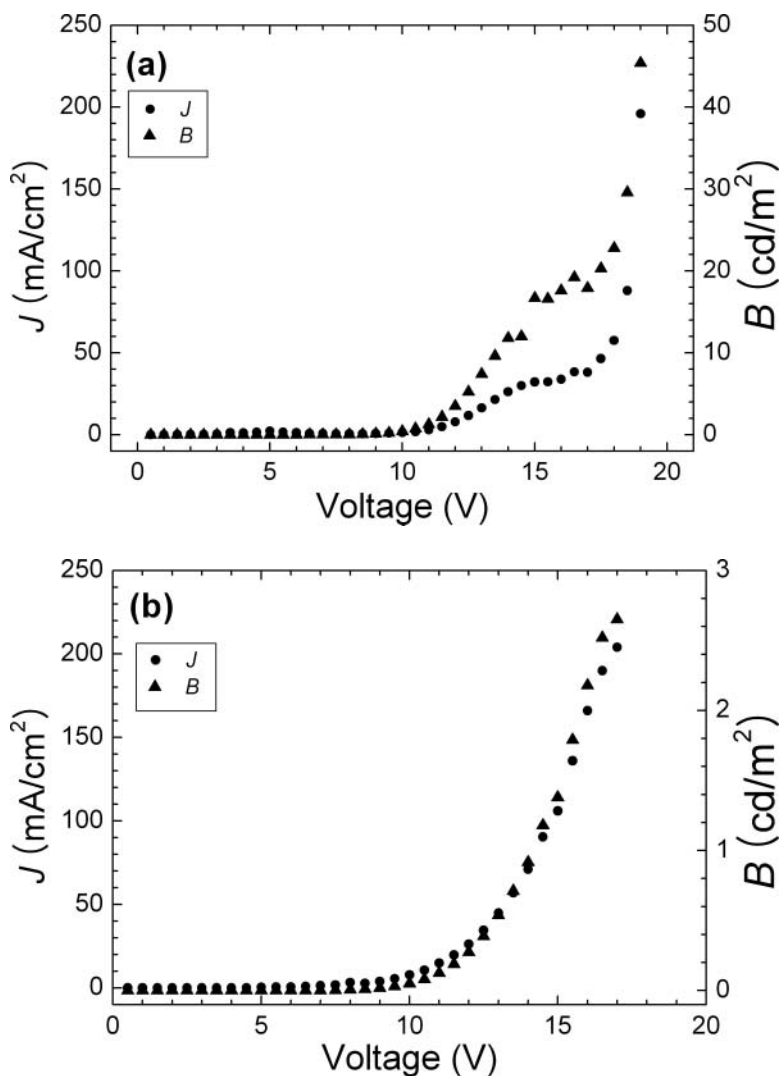


Figure 5. Current Density – Voltage – Brightness curves (a) ITO/PEDOT/PTOXDPF/Al and (b) ITO/PEDOT/PTPF/Al. (filled circle: current density – voltage, filled triangle: brightness – voltage)

potential of PTOXDPF is -5.13 eV, which is slightly higher than that of PTPF (-5.08 eV). Interestingly, OXD pendant does not affect the HOMO energy level significantly. This is presumably due to that the oxidation process in the polymer is dominated by phenothiazine building block and the delocalization of π -electrons is restricted in the main chain. From the estimated energy level data of PTOXDPF, we can expect that the hole injection ability from the anode to PTOXDPF and PTPF are almost same. The LUMO energy level of polymers is estimated from the HOMO energy level and band gap energy because the reduction process of polymers are not observed in the range from 0 to -3.0 V vs. Fc/Fc^+ . The LUMO energy level of PTOXDPF and PTPF are -2.16 and -2.34 eV, respectively.

Electroluminescent Properties

In order to investigate EL properties of the polymers, we fabricated the EL devices based on ITO/PEDOT:PSS(30 nm)/polymer (60 nm)/Al. The EL spectrum (Figure 4) of PTOXDPF and PTPF based device are almost identical to that of PL spectrum, indicating that the excited species of EL are same as the PL. of The current density and luminescence plotted as a function of applied voltage of the devices are shown in Figure 5. The turn-on voltages of brightness of PTOXDPF based device is 5.0 V, which are slightly higher than that of the device based on PT (4.5 V). The turn-on voltage of luminescence defined according to the literature [17] and figured out from log (current density) vs. voltage and log (luminescence) vs. voltage plot, respectively. This indicates that the hole injection efficiency from PEDOT:PSS to PTOXDPF is very similar that of PTPF. This result strongly supports the estimated HOMO energy level data from the cyclic voltammetry. The maximum brightness and efficiency of PTOXDPF based device (45.4 cd/m^2 and $5.21 \times 10^{-2} \text{ cd/A}$) are significantly higher than those of PTPF based device (2.65 cd/m^2 and $1.32 \times 10^{-3} \text{ cd/A}$). This presumably due to that OXD pendant improves the electron transporting in the emissive layer although the LUMO energy level of PTOXDPF is higher than PTPF.

Conclusions

We synthesized new π -conjugated alternating copolymer based on 10-hexylphenothiazine and 9,9-dihexylfluorene with aromatic OXD pendant through well known palladium catalyzed the Suzuki coupling reaction. In the optical properties, the position and shape of the UV-Vis and PL spectrum of PTOXDPF were blue-shifted than those of PTPF. This is due to that OXD pendant pendants impede formation of inter-chain excimer or aggregate. The HOMO energy level of PTOXDPF figured out from the CV were very similar to that of PTPF, indicating that ionization potential of the polymers dominated by phenothiazine building block. In spite of the LUMO energy level of PTOXDPF is higher than that of PTPF, the device efficiency based on PTOXDPF was significantly higher than that of the device based on PTPF. This indicates that OXD pendant improves electron transporting ability in the emissive layer.

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References

- [1] J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. Mackay, R. H. Friend, P. L. Burn, and A. B. Holmes, *Nature* **347**, 539 (1990).
- [2] J. H. Kim, J. H. Park, and H. Lee, *Chem. Mater.* **15**, 3414 (2003).
- [3] H. S. Kim, S. M. Kang, and J. Y. Do, *Macromol. Res.*, **16**, 360 (2008).
- [4] Y. H. Kim, S. J. Park, J. W. Park, J. H. Kim, and S. K. Kwon, *Macromol. Res.*, **15**, 216 (2007).
- [5] Jiyoung Choi, Bong Lee, and Joo Hyun Kim, and Kyehwan Lee, *Macromol. Res.*, **17**, 319 (2009)
- [6] S.-H. Chen, Y. Chen, C.-S. Shiau, and C.-J. Tsai, *J. Polym. Sci., Part A: Polym. Chem.* **45**, 136 (2007).
- [7] H. Sun, C. Mei, Q. Zhou, Z. Liu, D. Ma, L. Wang, X. Jing, and F. J. Wang, *J. Polym. Sci., Part A: Polym. Chem.*, **44**, 3469 (2006).
- [8] S. A. Jenekhe, L. D. Lu, and M. M. Alam, *Macromolecules* **34**, 7315 (2001).
- [9] T. -Y. Wu and Y. Chen, *J. Polym. Sci., Part A: Polym. Chem.* **40**, 4452 (2002).
- [10] S. K. Lee, M. J. Cho, S. H. Lee, J. H. Kim, Q. Zhang, and D. H. Choi, *Macromol. Res.*, **12**, 484 (2004).
- [11] J. Choi, H. L. Choi, J. H. Kim, and B. Lee, *J. Korean Soc. Img. Sci. & Tech.*, **13**, 90 (2007).
- [12] J. Choi, D. Kim, B. Lee, J. H. Kim, and K. Lee, *Macromol. Res.*, **17**, 319 (2009).
- [13] A. Babel and S. A. Jenekhe, *Macromolecules* **36**, 8992 (2003).
- [14] J. H. Kim and H. Lee, *Synth. Met.* **144**, 169 (2004).
- [15] S. Janietz, D. D. C. Bradley, M. Grell, C. Gieberler, M. Inbasekaran, and E. P. Woo, *Appl. Phys. Lett.* **73**, 2453 (1998).
- [16] C. -C. Wu, J. C. Strum, R. A. Register, J. Tian,; E. P. Dana, and M. E. Thompson, *IEEE Trans. Electron Devices* **44**, 1269 (1997).
- [17] I. D. Parker, *J. Appl. Phys.* **75**, 1656 (1994).