Improvement of Efficiency in π-Conjugated Polymer Based on Phenothiazine by Introduction of Oxadiazole Pendant as a Side Chain

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Abstract: A new π-conjugated polymer, poly[(2-methoxy-(5-(2-(4-oxyphenyl)-5-phenyl-1,3,4-oxadiazole)-hexyloxy))-1,4-phenylene-1,2-ethenylene-*alt*-(10-hexyl-3,7-phenothiazine)-1,2-ethenylene] (PTOXDPPV), was synthesized by the Heck coupling reaction. The electron transporting unit, conjugated 1,3,4-oxadiazole (OXD), is attached on the main chain via linear 1,6-hexamethylenedioxy chain. The band gap and photoluminescence (PL) maximum of PTOXDPPV are 2.35 eV and 565 nm, respectively. These values are very close to those of poly[(2,5-didecyloxy-1,4-phenylene-1,2-ethenylene)-*alt*-(10-hexyl-3,7-phenothiazine)-1,2-ethenylene] (PTPPV), which does not have OXD pendant. The estimated HOMO energy level of PTOXDPPV was -4.98 eV, which is very close to that of PTPPV (-4.91 eV). The maximum wavelength of EL device based on PTOXDPPV and PTPPV appeared at 587 and 577 nm, respectively. In the PL and EL spectrum, the emission from OXD pendant was not observed. This indicates that the energy transfer from OXD pendants to main chain is occurred completely. The EL device based on PTOXDPPV (ITO/PEDOT/PTOXDPPV/Al) has an efficiency of 0.033 cd/A, which is significantly higher than the device based on PTPPV (ITO/PEDOT/PTPPV/Al) (4.28×10^{-3} cd/A). From the results, we confirm that the OXD pendants in PTOXDPPV facilitate hole-electron recombination processes in the emissive layer effectively.

Keywords: light-emitting diode, conjugated polymer, phenothiazine, aromatic oxadiazole.

Introduction

Since the first report of the polymer light emitting diode (PLED) by Friend group,[1] many researches have been done for improving the device efficiency and for tuning the emission color. 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),[2-7] 1,2,4-triazole (TAZ)[8-10] in the main chain or side chain to improve device efficiency. Because the most of π-conjugated polymers have good hole injection/transporting properties. In this paper, we report synthesis, optical, electrochemical, and electroluminescent properties of new phenothiazine based polymer containing OXD pendants (poly [(2-methoxy-(5-(2-(4-oxyphenyl)-5-phenyl-1,3,4-oxadiazole)-hexyloxy))-1,4-phenylene-1,2-ethenylene-*alt*-(10-hexyl-3,7-phenothiazine)-1,2-ethenylene], PTOXDPPV). Phenothia-

zine is very strong electron donor since it has sulfur atom.[11-13] In addition, phenothiazine based polymer reduces π-stacking since phenothiazine has highly nonplanar geometry.[14] However, phenothiazine based π-conjugated polymer has low efficiency since hole injection and transporting properties are superior to electron injection and transporting properties.[11,14-18] We attempt to improve EL efficiency of π-conjugated polymer based on phenothiazine by introducing OXD unit in the side chain, which has electron transporting properties. We also synthesized poly[(2,5-didecyloxy-1,4-phenylene-1,2-ethenylene)-*alt*-(10-hexyl-3,7-phenothiazine)-1,2-ethenylene] (PTPPV) to compare the optical and EL properties with PTOXDPPV. We investigated the fundamental optical and EL properties as well as the role of OXD in the improvement of EL efficiency of the polymer.

Experimental

Materials. Tetrahydrofuran (THF) was used after distillation over sodium/benzophenone. All other chemicals were purchased from Aldrich Chemical Co. or Tokyo Chemical

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Industry (TCI). All chemicals used as received unless otherwise described. 1,4-Didecyloxy-2,5-diiodobenzene (**4**) and 2-methoxy-{5-[2-(4-oxyphenyl)-5-phenyl-1,3,4-oxadiazole]-hexyloxy}-1,4-diiodobenzene (**5**) were synthesized according to the literature procedure.[5]

Synthesis of 10-hexyl-10*H*-phenothiazine (1). A portion of 40 mL of 50% NaOH aqueous solution (40 mL) were added into a solution of 10*H*-phenothiazine (10.0 g, 0.0500 mol) and benzyltriethylammonium chloride (30 mg) in DMSO (30 mL). *n*-Hexylbromide (9.94 g, 0.0600 mol) was added to the mixture. After 24 h, 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. The organic solvent removed in 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^+] 283. ^{1}H NMR (400 MHz, DMSO, ppm): δ 7.12: 7.12 (m, 4H), 6.96 (m, 2H), 1.64 (m, 2H), 1.35 (m, 2H), 1.21 (m, 4H), 0.80 (t, 3H).

Synthesis of 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 mixture was stirred for an hour at this temperature then slowly added into a solution of 10*H*-hexylphenothiazine (5.00 g, 17.6 mmol) in 80 mL of 1,2-dichloroethane at 4 °C. After complete addition of Vilsmeier reagent, the reaction mixture was stirred at 90 °C for 24 h. 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/MC (8/2). The light yellow liquid product yield was 4.52 g (75.5%). ^{1}H NMR (400 MHz, DMSO, 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).

Synthesis of 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 0 °C. After the completion of *n*-BuLi addition, the reaction mixture was stirred for 30 min at room temperature. The solution of 3.00 g (8.84 mmol) of compound **2** in 50 mL of anhydrous THF was added to above reaction mixture. The reaction mixture was gently refluxed for 4 h. After cooling to room temperature, the reaction mixture was 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/EA (8/2). The light yellow liquid product yield was 2.07 g (69.7%). MS [M^+]: 335. ^{1}H NMR (400 MHz, DMSO, 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).

Polymerization of PTPPV. PTPPV was synthesized by the Heck coupling reaction between **3** and **4** in DMF. A mixture of 0.500 mmol of compound **3**, 0.500 mmol of compound **4**, 3.4 mg (15 mmol) of Pd(OAc)$_2$, 30.4 mg (0.100 mmol) of tri-*o*-tolylphosphine and 0.31 mL of tributylamine in 10 mL of DMF was stirred at 120 °C for 24 h. 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 7.34-7.24 (br, Ar-*H*), 7.07-7.02 (br, Ar-*H*), 6.96-6.94 (br, Ar-*H*), 6.81-6.78 (br, vinyl-*H*), 4.03-4.01 (br, -OC*H*$_2$), 3.86-3.79 (br, N-C*H*$_2$), 1.88-1.79 (br, N-C*H*$_2$C*H*$_2$), 1.77-1.23 (br, -C*H*$_2$-), 1.24 (br, O(C*H*$_2$)$_9$C*H*$_3$), 0.85 (br, N-(C*H*$_2$)$_5$C*H*$_3$). ^{13}C NMR (100 MHz, CDCl$_3$, ppm): δ 151.00, 143.98, 139.71, 132.61, 128.64, 127.45, 126.80, 125.68, 125.10, 124.33, 121.94, 115.17, 110.58, 69.62, 47.72, 31.93, 29.71, 29.62, 29.49, 29.38, 22.71, 14.15, 14.00. Anal. Calcd. for C$_{48}$H$_{69}$NO$_2$S: C, 79.61; H, 9.60; N, 1.93; S, 4,42. Found: C, 81.28; H, 10.37; N, 2.14; S, 5.75.

Polymerization of PTOXDPPV. PTOXDPPV was synthesized by the Heck coupling reaction between **3** and **5** in DMF. Similar conditions were used as in the polymerization of PTPPV. ^{1}H NMR (400 MHz, CDCl$_3$, ppm): δ 8.05-7.47 (br, oxd-*H*), 7.34-7.24 (br, Ar-*H*), 7.07-7.02 (br, Ar-*H*), 6.96-6.94 (br, Ar-*H*), 6.81-6.78 (br, vinyl-*H*), 4.03-4.01 (br, -OC*H*$_2$ -OC*H*$_3$), 3.86-3.79 (br, N-C*H*$_2$), 1.88-1.79 (br, -OC*H*$_2$C*H*$_3$, N-C*H*$_2$C*H*$_2$), 1.77-1.23 (br, -C*H*$_2$-), 0.85 (br, -C*H*$_3$).). ^{13}C-NMR (100 MHz, CDCl$_3$, ppm): δ 164.57, 164.02, 161.89, 131.44, 128.99, 128.64, 126.79, 125.97, 124.09, 116.15, 115.18, 114.93, 69.41, 68.14, 56.26, 47.71, 31.45, 29.22, 26.61, 25.92, 22.61, 14.01. Anal. Calcd. for C$_{49}$H$_{51}$N$_3$O$_4$S: C, 75.64; H, 6.61; N, 5.40; S, 4.12. Found: C, 77.28; H, 7.15; N, 6.11; S, 5.25.

Measurements. The chemical structure of compounds was characterized by ^{1}H NMR spectra obtained using JEOL JNM ECP-400 spectrometer. The UV-Visible spectra of the polymers were measured using a UV-Visible Spectrophotometer (CARY100 CONC). Photoluminescence (PL) spectra of the polymers were obtained using a Fluorescence Spectrophotomerter (HITACHI F-4500). The EL spectra of the devices were obtained using a CCD array detector (Ocean Optics, USB4000). Cyclic voltammetry was carried out with EG&G 362 Scanning Potentiostat with a three electrode cell

in a solution of Bu₄NPF₆ (0.1 M) in freshly distilled MC at a scan rate 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 current-voltage (I-V) and EL intensity-voltage (EL-V) characteristics were measured using a current/voltage source and a luminometer (Minolta LS-500). UV-Visible and PL measurements and evaluation of EL devices were performed under ambient conditions.

EL Device Fabrication. The PEDOT:PSS (Baytron® P VP Al 4083) layer was prepared by spin-coating at a speed of 4,000 rpm followed by heat treatment at 140 °C for 10 min under nitrogen atmosphere. The polymer film was prepared by spin casting from the solution in chlorobenzene (20 mg/mL, 2,000 rpm) then dried under vacuum for 2 h. Prior to spin coating, the polymer solution was filtered through 0.2-μm membrane filters. Al electrode was deposited (150 to 200 nm) onto the surface of the spin-coated polymer film by the thermal evaporation technique at about 10⁻⁵ torr. The typical active area of the LED device was 4 mm².

Results and Discussion

The synthetic routes to the monomers and polymers are shown in Scheme I. 10-Hexyl-10H-phenothiazine-3,7-dicarbaldehyde (**2**) was synthesized from 10H-phenothiazine in two steps. The monomer, 10-hexyl-3,7-divinyl-10H-phenothiazine, was synthesized by wittig reaction between ylide of methyltriphenylphosphonium bromide and compound **2** in a yield of 69.7%. The polymers were synthesized by the well known Heck coupling reaction. All the polymers were characterized ¹H NMR spectroscopy. The number average molecular weight and polydispersity index (PDI) of PTPPV were 9,700 and 2.1. The value of PTOXDPPV were 10,200 and 1.6, respectively. In the TGA thermogram, the temperature of 5 wt% weight loss of PTPPV and PTOXDPPV appeared at 274 and 275 °C, respectively. In the DSC thermogram of the polymers, we could not observed glass transition behavior.

As shown in Figure 1, PTPPV solution in chloroform and film show absorption maximum at 440 and 443 nm, respectively. The PL maximum wavelength of PTPPV solution
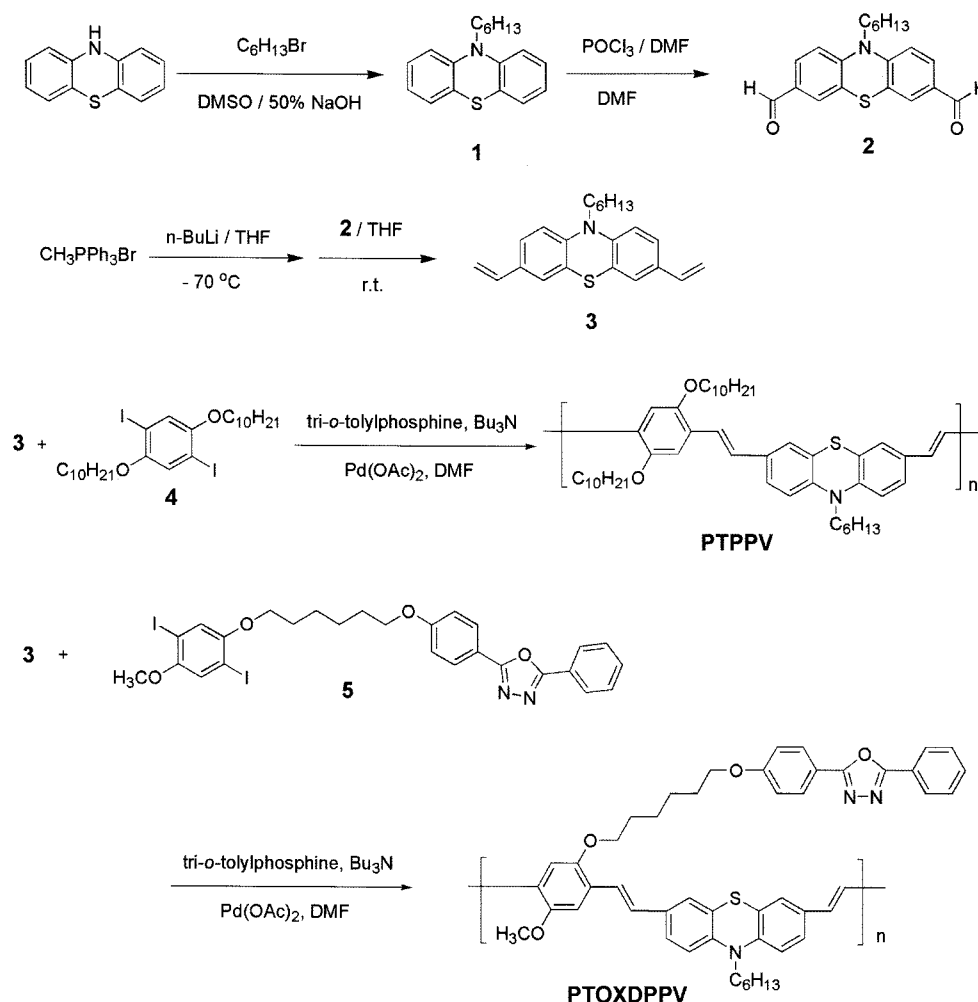
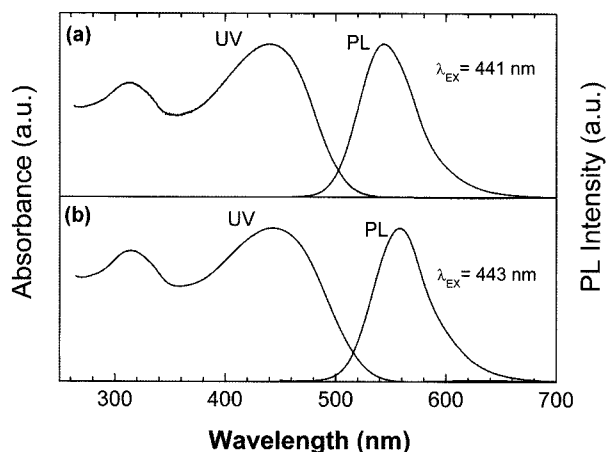**Scheme I.** Synthesis of monomers and polymers.

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

Figure 3. Cyclic voltammograms of PTPPV and PTOXDPPV.

and film are appeared at 542 and 556 nm, respectively. In case of MEH-PPV (poly(1-methoxy-4-ethylhexyloxy-2,5-phenylenevinylene), the PL maximum of the film was relatively large red-shifted (~35 nm) than that of solution.[19] However, the PL maximum of PTPPV film are slightly red-shifted (14 nm) than that of solution. Phenothiazine ring have highly nonplaner structure so that phenothiazine ring impede formation of interchain excimer or aggregate.[14] In the optical properties of PTOXDPPV, similar features are observed. The PL maximum of PTOXDPPV is 565 nm, which is slightly red-shifted (~17 nm) than that of PTOXDPPV solution. The band gap energy of PTOXDPPV is 2.35 eV, which is almost same as the band gap of PTPPV (2.36 eV). This indicates that the oxadiazole (OXD) pendant in PTOXD-PPV does not significantly affect the band gap energy, since hexamethylenedioxy spacer separate OXD unit from the main chain. When the PTOXDPPV solution is excited at 300 nm (Figure 2(a)), the PL spectrum shows weak emis-
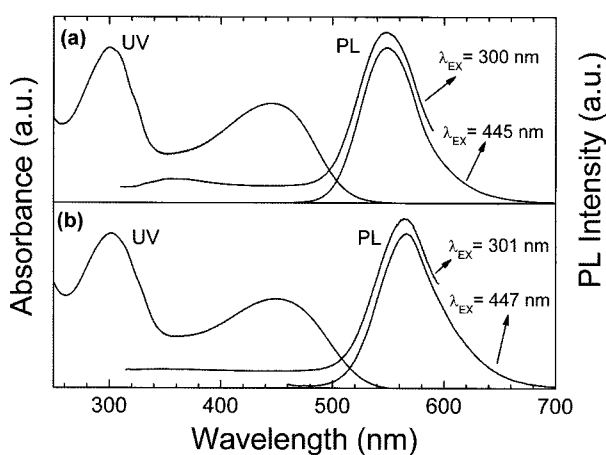
sion band around 340 nm, which corresponds to the emission of OXD pendant.[3,5] The energy transfer from OXD to the main chain of PTOXDPPV does not take place completely since OXD pendants are separated from the main chain via hexamethylenedioxy group. However, in the PTOXD-PPV film (Figure 2(b)) shows a broad emission band at 565 nm. It is believed that OXD pendant is allowed to contact the main chain leading to efficient energy transfer to the main chain.[20] The HOMO energy level of PTOXDPPV figured out from the onset oxidation potential of cyclic voltammogram (Figure 3) is -4.98 eV, which is similar to the HOMO energy level of PTPPV (-4.91 eV). One can also notice that OXD pendant in PTOXDPPV do not affect the HOMO energy level. We calculate the LUMO energy level from the HOMO energy level and optical band gap since the reduction potential of the polymers could not be observed up to -3.0 V vs. Ag/Ag^{+}. The electro-optical properties of polymers were summarized in Table I.

Figure 2. UV-Vis and PL spectrum of PTOXDPPV (a) solution in chloroform and (b) film (PL spectra are offset for clarity).

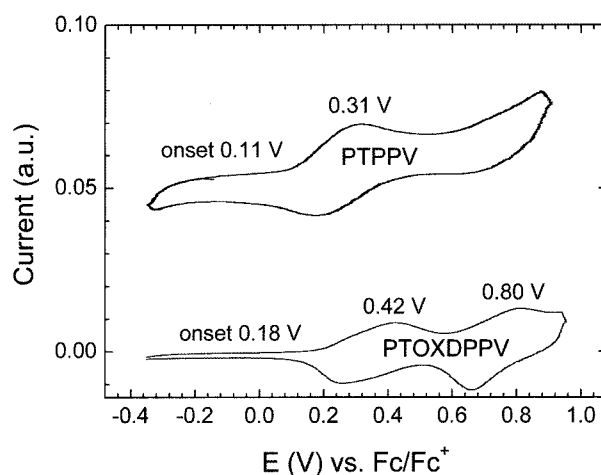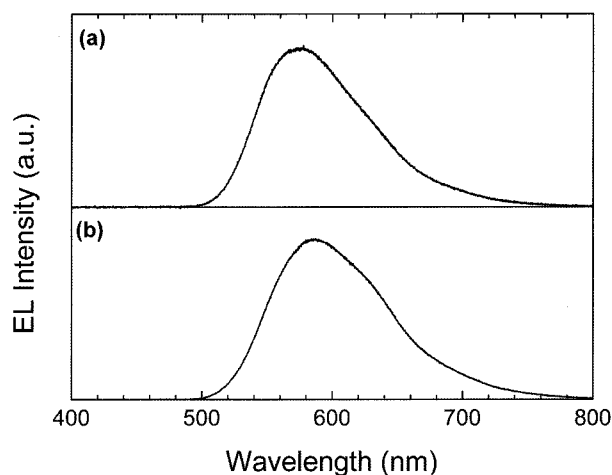**Figure 4.** EL spectra of (a) ITO/PEDOT/PTPPV/Al and (b) ITO/PEDOT/PTOXDPPV/Al.

Table I. Electro-Optical Properties of Polymers

	Solution		Film		E_g^a (eV)	HOMO[b] (eV)	LUMO[c] (eV)
	UV_{max} (nm)	PL_{max} (nm)	UV_{max} (nm)	PL_{max} (nm)			
PTPPV	440	542	443	556	2.36	-4.91	-2.57
PTOXDPPV	445	548	447	565	2.35	-4.98	-2.63

$^a E_g$ (bandgap) figured out from the absorption edge of UV-Vis spectrum.
^{b}HOMO energy level determined from the onset potential of oxidation by assuming the absolute energy level of ferrocene to be 4.8 eV.
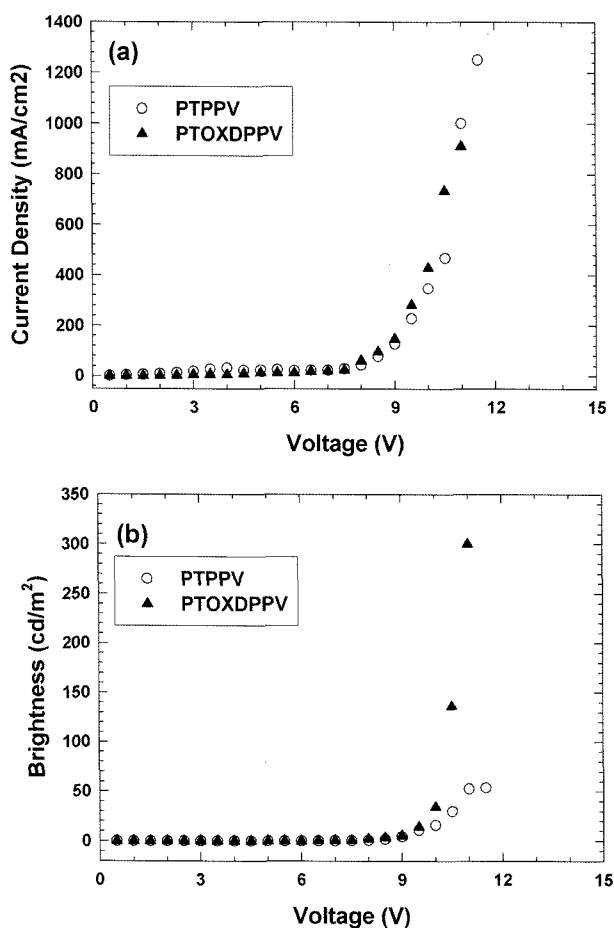^{c}LUMO energy level estimated from the HOMO energy level and band gap.

Figure 5. (a) Current density - voltage and (b) brightness - voltage curves of ITO/PEDOT/PTPPV/Al (circle) and ITO/PEDOT/PTOXD-PPV/Al (filled triangle).

As shown in Figure 4, the EL maximum of the device based on PTOXDPPV (ITO/PEDOT/PTOXDPPV/Al) and PTPPV (ITO/PEDOT/PTPPV/Al) appear at 587 and 577 nm, respectively. As shown in Figure 5, typical rectification characteristics are observed in the devices. The turn on voltage[21] of current of the device based on PTPPV is 7.0 V, which is slightly lower than PTOXDPPV device (7.5 V). However, the turn on voltage of brightness of the device based on PTOXD-PPV is 8.0 V, which is slightly lower than the device based on PTPPV (8.5 V). This is presumably due to the OXD pendants facilitate electron injection. The device based on

PTOXDPPV has an efficiency of 0.033 cd/A at a current density of 909 mA/cm², which is significantly higher than that of the device based on PTPPV (4.28×10^{-3} cd/A at a current density of 1,250 mA/cm²). Maximum brightness of PTOXDPPV based device is 300 cd/m², which is higher than that of PTPPV based device (54 cd/m²). From the results, we confirm that the OXD pendants in PTOXDPPV facilitate hole-electron recombination processes in emissive layer effectively. In addition, the presence of bulky OXD pendants improves the device efficiency by reducing the possibility of inter-chain exciton quenching.

Conclusions

We synthesized a new phenothiazine based polymer with OXD units by the Heck coupling reaction. In the optical and electrochemical properties, the OXD pendants did not affect PL and EL maximum in comparison with PTPPV. The efficiency of the device based on PTOXDPPV was significantly higher than the device based on PTPPV. It was suggested that the hole-electron recombination processes were facilitated in the emitting layer by the OXD pendants.

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