

Synthesis and Characterization of 1,2,4-Oxadiazole-Based Deep-Blue and Blue Color Emitting Polymers

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Two donor-acceptor-donor monomers such as 3,5-bis(4-bromophenyl)-1,2,4-oxadiazole (BOB) and 3,5-bis(5-bromothiophen-2-yl)-1,2,4-oxadiazole (TOT) incorporating electron transporting and hole blocking 1,2,4-oxadiazole moiety were copolymerized with light emitting fluorene derivative *via* Suzuki polycondensation to afford two new polymers, **PFBOB** and **PFTOT**, respectively. The optical studies for polymers **PFBOB** and **PFTOT** revealed that the band gaps are 3.10 eV and 2.72 eV, respectively, and polymer **PFBOB** exhibited a deep-blue emission while polymer **PFTOT** showed blue emission in chloroform and as thin film. The photoluminescence quantum efficiencies (Φ_f) of polymers **PFBOB** and **PFTOT** in chloroform calculated against highly blue emitting 9,10-diphenylanthracene (DPA, $\Phi_f = 0.90$) were 1.00 and 0.44, respectively.

Key Words : Copolymers, 1,2,4-Oxadiazole, Fluorene, Blue emissive polymers

Introduction

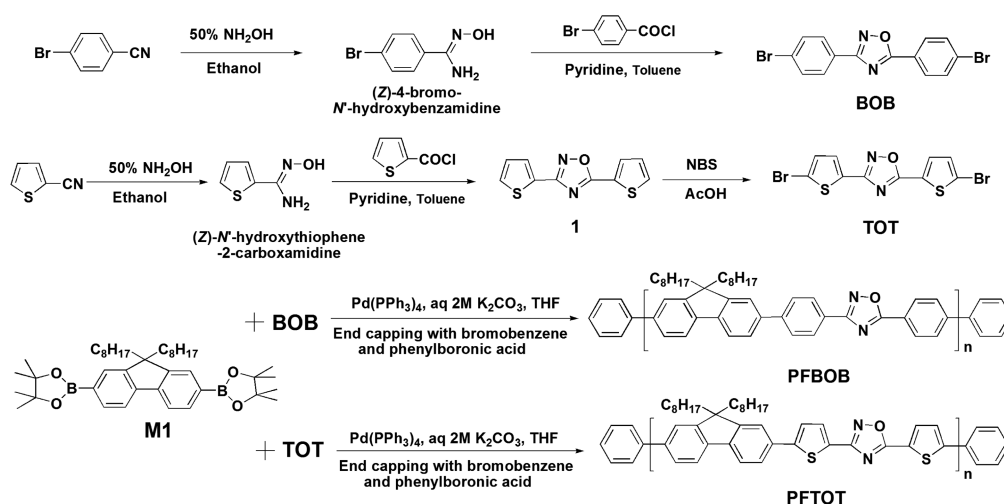
Recently, various π -conjugated polymers have been developed for their applications in polymer light-emitting diodes (PLEDs), organic photovoltaics (OPVs), photodetectors, chemosensors and organic thin film transistors (OTFT).¹ For example, fluorene-based polymers have been developed for PLED applications since fluorene-based polymers show balanced carrier mobility, high photo and electroluminescence (PL and EL) efficiencies, good thermal and chemical stabilities.² In addition, fluorene-based polymers have been developed for fluorogenic chemosensors for the selective detection of various metal ions.³ It is well known that the light-emitting properties of fluorene-based polymers are usually tuned by incorporating different π -conjugated chromophores on their main chain.⁴⁻⁸ The tunable light-emitting properties of fluorene-based polymers might be the reason for their wide applications in PLEDs and fluorogenic chemosensors.

Many studies on the introduction of charge transporting moieties into π -conjugated polymers for efficient PLEDs have been reported.⁴⁻⁸ However, most of the emissive π -conjugated polymers are π -excessive in nature, and consequently, those polymers are found to transport the holes more efficiently than electrons. The charge imbalance of the π -conjugated polymers is considered as the most important limiting factor for the PLEDs device performances.⁹ To solve those issues, previously electron transporting layer was incorporated in between the light-emitting and cathode layers and also low-work function metals were used as an cathodes with the aim of improving the electron injection from light emitting layer to cathode, and consequently, enhanced electron injection from light emitting layer to cathode gave improved EL efficiency for π -excessive polymer based PLEDs.¹⁰ But, incorporating the efficient electron

transporting layer or constructing the multilayer structured PLEDs are practically quite difficult. To overcome those issues, synthesizing light-emitting polymers showing high electron affinity (n-dope type polymers) is crucial because those polymers itself transport the electron quite well, and consequently, might offer highly efficient PLEDs without any electron transporting layer. Previously strong electron accepting 1,3,4-oxadiazole unit was incorporated in polymer main chain and the resulting n-dope type polymers were successfully used as light emitting¹¹⁻¹⁹ and electron transporting^{20,21} layers in the PLEDs preparation. In addition, polymers containing 1,3,4-oxadiazole unit have been successfully utilized as fluorogenic chemosensors for the selective detection of metal ions.²²⁻²⁴ However, polymers containing 1,2,4-oxadiazole unit in polymer main chain have not been utilized. As an effort to investigate the light emitting properties of 1,2,4-oxadiazole-based n-dope type polymers, two monomers such as 3,5-bis(4-bromophenyl)-1,2,4-oxadiazole (BOB) and 3,5-bis(5-bromothiophen-2-yl)-1,2,4-oxadiazole (TOT) were copolymerized with light emitting fluorene derivative to afford two new polymers **PFBOB** and **PFTOT**. In this paper, we present the detailed synthesis and the optical and electrochemical properties of polymers **PFBOB** and **PFTOT**.

Experimental

Materials and Instruments. The commercially available reagents were purchased from Aldrich and used without further purification. The NMR spectra were recorded using a 300-MHz Varian Mercury Plus spectrometer. The weight molecular weight (M_w) and polydispersity (*PDI*) of the polymers were analyzed by using gel permeation chromatography (GPC) on Agilent 1260 Infinity Series separation module with chloroform as an eluent and with polystyrene



Scheme 1. Synthetic route to polymers PFBOB and PFTOT.

as a calibration standard. Thermogravimetric analysis was performed by using a Mettler Toledo TGA/SDTA 851 analyzer. The absorption and photoluminescence spectra were recorded using a JASCO V-570 and Hitachi F-4500 fluorescence spectrophotometers, respectively. The CV analyses were performed by using CH Instruments Electrochemical Analyzer.

Synthesis of 3,5-Di(thiophen-2-yl)-1,2,4-oxadiazole (1). To a stirred solution of thiophene-2-carbonitrile (2.5 g, 23.0 mmol) in ethanol (40 mL) was added 50% aqueous hydroxylamine solution (3 mL). The mixture was heated to reflux for 2 h. Then, the solvent was removed by rotary evaporation and the residue was dissolved in ethyl acetate (100 mL) and washed one time with water (20 mL). The organic layer was separated and dried over anhydrous Na₂SO₄. After filtration and removal of the organic solvent by rotary evaporation, (Z)-N'-hydroxythiophene-2-carboxamidine was obtained as a white solid. Yield: 3.0 g (92%). mp 96-97 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.32 (dd, 1 H), 7.29 (dd, 1 H), 7.05 (dd, 1 H), 4.89 (brd s, 2 H). (Z)-N'-Hydroxythiophene-2-carboxamidine (2.5 g, 17.6 mmol) was dissolved in 50 mL of toluene and the solution was cooled to 0 °C. After 15 min, pyridine (1.45 mL, 18 mmol) and 2-thiophenecarbonyl chloride (1.92 mL, 18 mmol) were added and stirred for 2 h at 0 °C. Then, the ice bath was removed and the mixture was refluxed for 15 h. The insoluble material was filtered off in hot condition and the filtrate was concentrated by rotary evaporation. The crude material was purified by column chromatography (silica gel, hexane:ethyl acetate, 90:1, v/v) to afford pure compound **1** as a white solid. Yield: 3.5 g (93%). mp 131-132 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.96 (dd, 1 H), 7.86 (dd, 1 H), 7.67 (dd, 1 H), 7.52 (dd, 1 H), 7.22 (dd, 1 H), 7.17 (dd, 1 H); ¹³C NMR (75 MHz, CDCl₃) δ 132.4, 132.3, 130.0, 129.6, 128.8, 128.2; HRMS (EI⁺, *m/z*) [M⁺] Calcd for C₁₀H₆N₂OS₂ 233.9922, found 233.9926.

Synthesis of 3,5-Bis(5-bromothiophen-2-yl)-1,2,4-oxadiazole (TOT). To a stirred solution of compound **1** (1.0 g,

4.3 mmol) in acetic acid (30 mL) was added *N*-bromo-succinimide (NBS) (2.3 g, 12.9 mmol) in one portion. The solution was slowly heated to 70 °C and stirred for 6 h. Then, the solution was cooled to room temperature and poured into water (100 mL). The mixture was extracted with ethyl acetate for three times (25 mL × 3) and the combined organic layer was washed once with brine (100 mL) and dried over anhydrous Na₂SO₄. The solution was filtered and evaporated by rotary evaporation and the crude product was purified by column chromatography (silica gel, hexane:methylene chloride, 80:20, v/v) to afford pure TOT as a yellowish solid. Yield: 0.9 g (54%). mp 122-123 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.69 (d, 1 H), 7.58 (d, 1 H), 7.18 (d, 1 H), 7.13 (d, 1 H); ¹³C NMR (75 MHz, CDCl₃) δ 132.6, 131.8, 131.2, 130.4; HRMS (EI⁺, *m/z*) [M⁺] Calcd for C₁₀H₄Br₂N₂OS₂ 389.8132, found 389.8134.

Synthesis of Polymers PFBOB and PFTOT. A solution of BOB (0.15 g, 0.4 mmol), which was prepared *via* the known method,²² and **M1** (0.26 g, 0.4 mmol) for PFBOB or a solution of TOT (0.16 g, 0.4 mmol) and **M1** (0.26 g, 0.4 mmol) for PFTOT in THF (40 mL) was purged well with argon for 45 min. To the degassed solution, Pd (PPh₃)₄ (0.02 g, 5 mol %) and aq. 2 M K₂CO₃ (7 mL) were added under argon atmosphere and then the reaction mixture was refluxed for 48 h. Then, 50 mg of phenylboronic acid was added and the mixture was refluxed again. After 6 h, 0.1 mL of bromobenzene was added and refluxed for 6 h. The reaction mixture was cooled to room temperature and then the mixture was added into the stirred mixed solvent of methanol:water (100 mL:50 mL). The crude polymers were purified by Soxhlet extraction with methanol for 24 h and acetone for 24 h to afford polymers PFBOB and PFTOT, respectively. **PFBOB:** Yield: 0.21 g (70%). ¹H NMR (300 MHz, CDCl₃) δ 8.28-8.40 (m, 4 H), 7.80-7.94 (m, 6 H), 7.62-7.74 (m, 4 H), 2.00-2.20 (m, 4 H), 1.00-1.24 (m, 24 H), 0.70-0.88 (m, 6 H). **PFTOT:** Yield: 0.24 g (73%). ¹H NMR (300 MHz, CDCl₃) δ 7.30-8.04 (m, 10 H), 1.92-2.16 (m, 4 H), 0.90-1.30 (m, 24 H), 0.66-0.88 (m, 6 H).

Results and Discussion

The synthetic route for the synthesis of monomers (BOB and TOT) and polymers (PFBOB and PFTOT) are outlined in Scheme 1. Monomer BOB was synthesized from the commercially available 4-bromobenzonitrile as shown in Scheme 1 *via* the procedure reported.²⁵ Monomer TOT was prepared *via* the similar procedure. Thiophene-2-carbonitrile was treated with 50% aqueous hydroxylamine solution to afford (*Z*)-*N*'-hydroxythiophene-2-carboximidine. The amidine derivative was treated with thiophene-2-carbonyl chloride at 0 °C to afford O-acylated intermediate and then the intermediate was cyclized to 1,2,4-oxadiazole to afford 3,5-di-(thiophen-2-yl)-1,2,4-oxadiazole (**1**) by refluxing in toluene. The selective dibromination of compound **1** by using *NBS* in acetic acid offered monomer TOT. Light emitting co-monomer M1 was synthesized according to the procedure reported.⁵ The Suzuki polycondensation reaction between monomer M1 and BOB or monomer M1 and TOT followed by end capping afforded two new alternating copolymers PFBOB and PFTOT, respectively.

The weight average molecular weight (M_w) and the polydispersity (*PDI*) of the polymers PFBOB and PFTOT were estimated from the GPC analysis to be 2.02×10^4 , 1.72 and 1.63×10^4 , 1.78, respectively. Polymers PFBOB and PFTOT exhibited good solubility in chlorinated solvents such as chloroform, chlorobenzene, dichlorobenzene. The 5% weight loss temperature of polymers PFBOB and PFTOT was determined to be 407 °C and 415 °C, respectively, from the thermogravimetric analysis (TGA) analysis. The TGA analysis revealed that the polymers PFBOB and PFTOT are stable enough for opto-electronic applications. The TGA curves for polymers PFBOB and PFTOT are presented in Figure 1.

The solution (chloroform) and film (on glass) state absorption spectra of polymers PFBOB and PFTOT were measured and compared with that of 9,10-diphenylanthracene (DPA) as the calibration standard,²⁶ as shown in Figure 2. The structure of DPA is presented in Figure 3. The absorption maxima of polymers PFBOB and PFTOT in solution were identical with those as thin film. The maximum absorp-

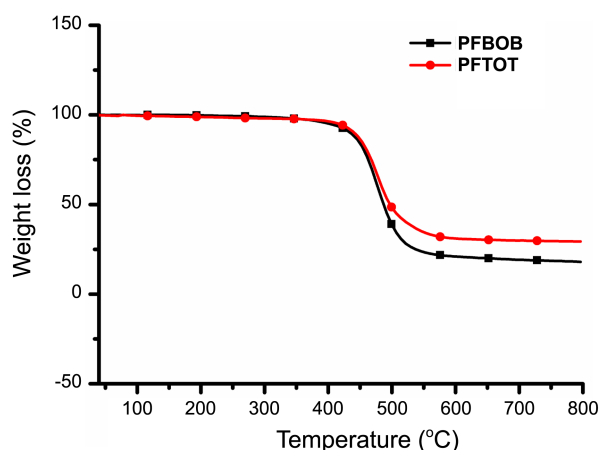


Figure 1. TGA curves of PFBOB and PFTOT.

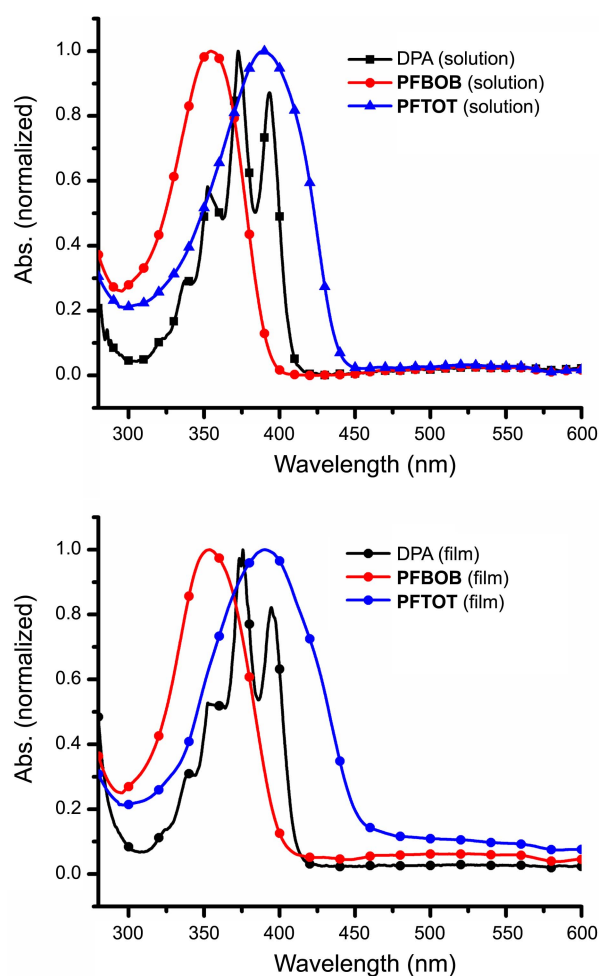
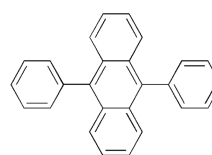


Figure 2. Absorption spectra of PFBOB, PFTOT and standard 9,10-diphenylanthracene (DPA) in chloroform and as thin film on glass.

tions of polymers PFBOB and PFTOT were appeared at 354 nm and 390 nm, respectively. The absorption maximum of polymer PFTOT was red shifted by 43 nm compared with that of polymer PFBOB. The absorption maxima of BOB and TOT were found to be located at 260 nm and 298 nm, respectively, and, consequently, the red shifted absorption maximum of PFTOT compared with that of PFBOB is expected to be stemmed from the TOT unit. Interestingly, the absorption band of polymer PFBOB was found be quite narrow and blue shifted compared with that of DPA, whereas polymer PFTOT showed red shifted absorption band compared with that of DPA. In addition, polymer PFBOB and PFTOT displayed single absorption maximum while DPA showed several absorption maxima at high energy part



9,10-diphenylanthracene (DPA)

Figure 3. Molecular Structure of DPA.

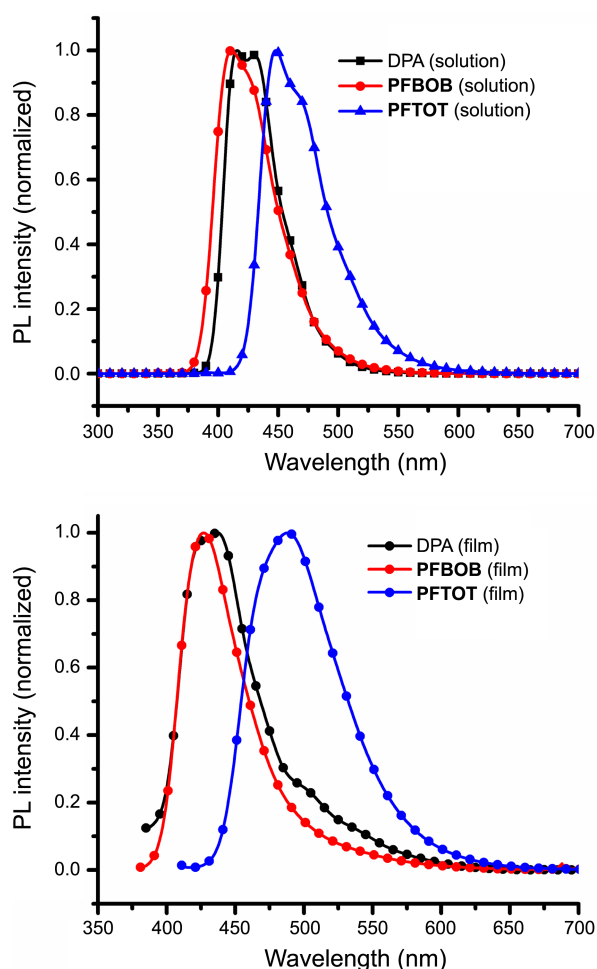


Figure 4. Photoluminescence spectra of **PFBOB**, **PFTOT** and **DPA**.

of the solar spectra. The optical band gap ($E_{g,opt}$) of polymers **PFBOB** and **PFTOT** was calculated to be 3.10 eV and 2.72 eV, respectively, which is 0.11 eV lower and 0.26 eV higher, respectively, than that of **DPA**.

The photoluminescence (PL) measurements of polymers **PFBOB**, **PFTOT** and **DPA** were carried out in chloroform and as thin film on glass with photo excitation at their respective absorption maximum. Their corresponding PL spectra of polymers **PFBOB** and **PFTOT** are displayed in Figure 4. Polymer **PFBOB** exhibited deep blue emission with maximum emission at 411 nm in solution and 427 nm as film. On the other hand, polymer **PFTOT** showed blue

emission with maximum emission at 448 nm in solution and 488 nm as film. The PL maximum of **DPA** was found to be appeared at 416 nm in solution and 437 nm as film. The emission maximum of polymer **PFBOB** was found to be slightly blue shifted compared with that of **DPA** whereas that of polymer **PFTOT** was found to be slightly red shifted and the comparison of the PL spectra are presented in Figure 4. The PL efficiencies of polymers **PFBOB** and **PFTOT** in solution were measured by comparing with that of standard **DPA**. The PL quantum efficiencies (Φ_f) of polymers **PFBOB** and **PFTOT** in chloroform were found to reach as high as 1.00 for **PFBOB** and 0.44 for **PFTOT** compared with that of **DPA** ($\Phi_f = 0.90$, in chloroform) as the standard. In comparison with PFs² and structurally quite similar polymers containing 1,3,4-oxadiazole moiety,^{12,13,19} polymer **PFBOB** showed quite narrow and only blue emission PL band with blue shifted emission maximum.

The electrochemical properties of the polymers **PFBOB** and **PFTOT** were studied by using cyclic voltammetry (CV) analysis. The CV analysis were performed with each of polymers **PFBOB** and **PFTOT** in chloroform containing three electrodes such as Ag/AgCl (reference electrode), platinum (working and counter electrode) and tetrabutylammonium tetrafluoroborate (0.1 M supporting electrolyte, Bu₄NBF₄). The CV spectra of the polymers **PFBOB** and **PFTOT** are shown in Figure 5. The onset oxidation ($E_{ox,onset} = 1.50$ V and 0.98 V, respectively) and reduction ($E_{red,onset} = -1.68$ V and -1.72 V, respectively) potential of polymers **PFBOB** and **PFTOT** were determined from the CV spectra presented in Figure 5. The energy levels (HOMO and LUMO) of polymers **PFBOB** and **PFTOT** were calculated by using the standard equations as follows: $E_{HOMO} = [-(E_{ox,onset} vs. Ag/AgCl - E_{onset,ferrocene} vs. Ag/AgCl) - 4.8]$ eV and $E_{LUMO} = [-(E_{red,onset} vs. Ag/AgCl - E_{onset,ferrocene} vs. Ag/AgCl) - 4.8]$ eV, where $E_{(onset ferrocene vs. Ag/AgCl)}$ is 0.51 V and the value of 4.8 eV is the energy level of ferrocene. The HOMO and LUMO energy levels of polymer **PFBOB** were calculated to be -5.79 eV and -2.61 eV, respectively, and those of polymer **PFTOT** were calculated to be -5.27 eV and -2.57 eV, respectively. The electrochemical band gaps ($E_{g,elec}$) of polymers **PFBOB** and **PFTOT** were determined from the HOMO and LUMO energy levels to be 3.18 eV and 2.70 eV, respectively. The electrochemical band gap value was found to be quite similar with that of the optical band gap values. The optical and electrochemical properties of polymers **PFBOB** and **PFTOT** discussed are summarized in Table 1.

Table 1. Summary of the optical and electrochemical properties of polymers **PFBOB** and **PFTOT**

Polymer	λ_{max} in solution (nm) ^a	λ_{max} as film (nm) ^b	$E_{g,opt}$ (eV) ^c	PL _{max} in solution (nm) ^d	PL _{max} as film (nm) ^e	$(\Phi_f)^f$	HOMO (eV) ^g	LUMO (eV) ^h	$E_{g,elec}$ (eV) ⁱ
PFBOB	354	354	3.10	411	427	1.00	-5.79	-2.61	3.18
PFTOT	390	390	2.72	448	488	0.44	-5.27	-2.57	2.70

^aAbsorption maximum of the polymers in chloroform. ^bAbsorption maximum of the polymers as thin film on the glass substrate. ^cThe optical band gap estimated from the onset wavelength of the optical absorption as thin film. ^dPhotoluminescence maximum of the polymers in chloroform. ^ePhotoluminescence maximum of the polymers as thin film on the glass substrate. ^fThe quantum efficiency calculated against the standard, 9,10-diphenylanthracene (9,10-DPA), in chloroform. ^gThe HOMO level of the polymers estimated from cyclic voltammetry analysis. ^hThe LUMO level of the polymers calculated from cyclic voltammetry analysis. ⁱThe electrochemical band gap calculated by using the equation of $E_{g,elec} = \text{HOMO} - \text{LUMO}$.

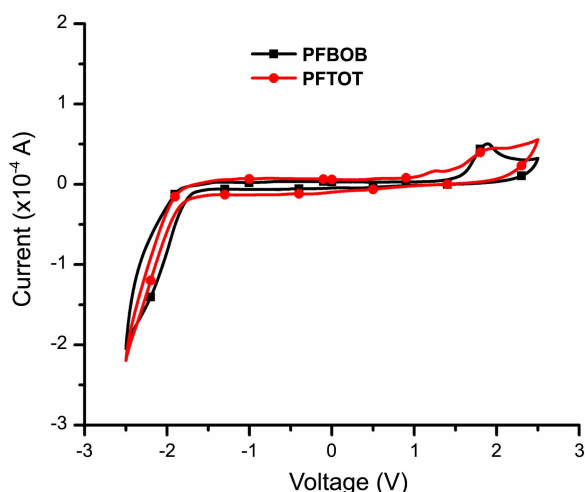


Figure 5. Cyclic voltammogram of PFBOB and PFTOT.

Conclusion

In summary, two new π -conjugated polymers (PFBOB and PFTOT) containing 1,2,4-oxadiazole moiety and light emitting fluorene unit were prepared. The PL measurements indicated that polymer PFBOB exhibited a deep-blue emission, while polymer PFTOT showed blue emission both in chloroform and as thin film. The photoluminescence quantum efficiencies (Φ_f) of polymers PFBOB and PFTOT in chloroform were as high as 1.00 and 0.44, respectively, calculated against 9,10-diphenylanthracene (DPA, $\Phi_f = 0.90$). However, polymers PFBOB and PFTOT were found to show negligible EL properties. In this instance, polymers PFBOB and PFTOT are concluded to be not suitable for the application in PLEDs, but they are expected to be utilized, for example, as polymer fluorophores for the preparation of fluorogenic polymer chemosensors because of their high photoluminescence quantum efficiencies.

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