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Synthesis and Characterization of π-Conjugated Polymers Based on 2-arylbenzimidazole and 4,7-di-thiophene-2-yl-4,5,6,7-tetrahydro-benzo[1,2,5]thiadiazole

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Synthesis and Characterization of π-Conjugated Polymers Based on 2-arylbenzimidazole and 4,7-di-thiophene-2-yl-4,5,6,7-tetrahydro-benzo[1,2,5]thiadiazole

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A newly designed 2-arylbenzimidazole derivative which plays a role of co-acceptor unit has been prepared for the synthesis of conjugated polymer. 2-arylbenzimidazole derivative has been incorporated into 4,7-dithiophen-2-yl-benzo(2,1,3)thiadiazole (TBT) and fluorene based alternating copolymers with different ratios of 5 mol.% and 10 mol.% named POFTBT-IMD5, POFTBT-IMD10, respectively. We also synthesized alternating copolymer of 9,9-dioctylfluorene and TBT (POFTBT) to compare physical properties. POFTBT-IMD5, POFTBT-IMD10 films showed absorption peaks at 559 and 555 nm, respectively. The HOMO and LUMO energy levels of POFTBT-IMD5, POFTBT-IMD10 were −5.4/−3.84 eV and −5.4/−3.81 eV, respectively, which were similar to those of POFTBT (−5.3/−3.7 eV).

Key words 2-arylbenzimidazole; benzothiadiazole; conjugated polymer; low band gap

Introduction

Polymer solar cells (PSCs), especially bulk-hetero-junction (BHJ) PSCs comprising π-conjugated (semiconducting) polymers and fullerene derivatives have attracted an increasing amount of attention in the research community due to their advantages over traditional silicon-based solar cells for their low cost, light weight, and the facility for solvent process [1,2].

During the past decade, regioregular poly(3-hexylthiophene) (P3HT) was applied generally in organic photovoltaic cells because of its high carrier mobility. However, it was not ideal material for polymer solar cell to improve the solar spectrum harvest [3]. To achieve highly efficient PSCs, polymer material should have low band gap, high charge carrier

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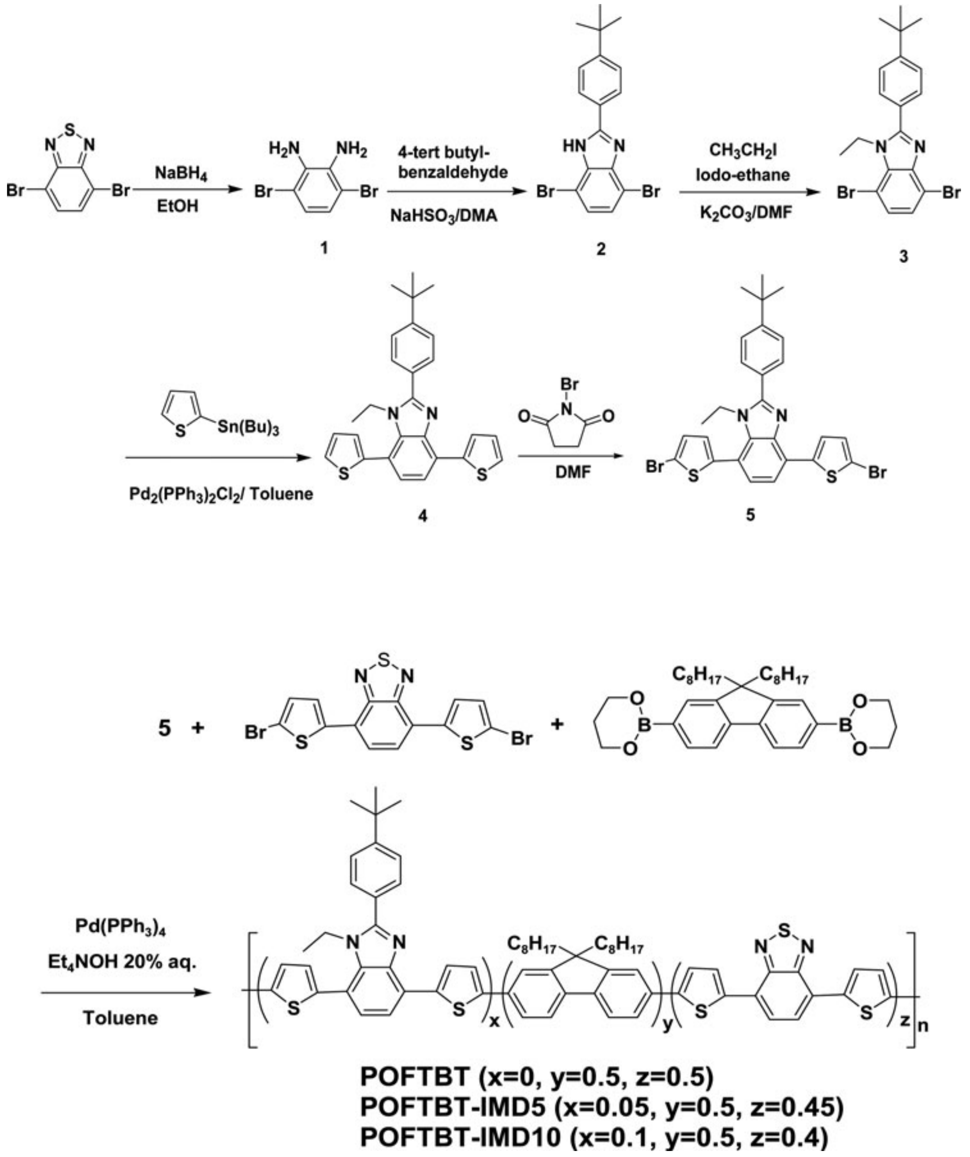
mobility, relatively low HOMO level, high molecular weight, and good solubility [4]. To meet all these requirements, one of the strategies is the synthesis of alternating copolymer from electron-rich (donor) and electron-deficient (acceptor) units.

In this work (as shown in Scheme 1), we report the syntheses and characterization of new conjugated small molecules containing electron-rich–electron-poor pairs utilizing 2-arylbenzimidazole derivative, 4,7-dibromo-2,1,3- benzothiadiazole and 9,9-dioctylflourence based copolymer.



Scheme 1. Synthetic routes to monomers and polymers.

Experimental

Synthesis

3,6-Dibromo-benzene-1,2-diamine (1). To a suspension of 4,7-dibromo-2,1,3-benzothiadiazole (4.41 g, 15 mmol) in ethanol (150 mL) was added slowly sodium borohydride ($NaBH_4$, 6.81 g, 0.18 mol) at 0°C, and the mixture was stirred for 12 h at room temperature. After evaporation of the solvent, 200 mL of water was added, and the mixture was extracted with diethylether. The extract was dried over anhydrous magnesium sulfate ($MgSO_4$), evaporated the solvent and then recrystallized by hexane; a white solid compound was obtained (2.99 g, 75%). MS: [M^+], m/z 604. ^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ 6.82 (s, 2H), 3.88 (s, 4H).

4,7-Dibromo-2-(4-tert-butyl-phenyl)-1H-benzoimidazole (2). 4-tert butylbenzaldehyde (1.8 mL, 10.5 mmol) was added dropwise to a mixture of 3,6-Dibromo-benzene-1,2-diamine (2.66 g, 10 mmol) and sodium hydrogen sulfite ($NaHSO_3$, 1.04 g, 10 mmol) in Dimethylacetamide (DMA, 10 mL) at 100°C. The mixture was refluxed at 100°C for 4 h on an oil bath. After cooling the mixture to room temperature, a portion of 100 mL of water was added and the mixture was extracted with ethyl acetate. The combined organic phase was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The crude product was purified through column chromatography using hexane/ethyl acetate (4/1, volume ratio) to provide 4,7-Dibromo-2-(4-tert-butyl-phenyl)-1H-benzoimidazole as a white solid (3.31 g, 81%). MS: [M^+], m/z 604. ^{1}H-NMR (400 MHz, DMSO, ppm): δ 9.3 (s, 1H), 8.27–8.25 (d, $J = 8.4$ Hz, 2H), 7.60–7.58 (d, $J = 8.4$ Hz, 2H), 3.37 (s, 2H), 1.34 (s, 9H).

4,7-Dibromo-2-(4-tert-butyl-phenyl)-1-ethyl-1H-benzoimidazole (3). 4,7-Dibromo-2-(4-tert-butyl-phenyl)-1H-benzoimidazole (3.27 g, 8 mmol) was dissolved in 20 mL of dimethyl formamide (DMF) and stirred vigorously with potassium carbonate (K_2CO_3, 3.32 g, 24 mmol) at room temperature for an hour. The mixture of ethyl iodine (C_2H_5I, 1.29 mL, 16 mmol) in 10 mL of DMF was added dropwise with dropping funnel at 50°C and then the mixture was stirred for 6 h. After cooling the mixture to room temperature, 100 mL of water was added and the mixture was extracted with ethyl acetate. The organic phase was collected and dried by anhydrous $MgSO_4$. Removal of the solvent and column purification on silica gel using hexane and ethyl acetate mixed eluent (10/1, volume ratio) yielded 4,7-Dibromo-2-(4-tert-butyl-phenyl)-1-ethyl-1H-benzoimidazole as a white solid (3.0 g, 86%). MS: [M^+], m/z 604. ^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ 7.59–7.57 (d, $J = 8.4$ Hz, 2H), 7.52–7.49 (d, $J = 8.4$ Hz, 2H), 7.32–7.30 (d, $J = 8.4$ Hz, 1H), 7.28–7.26 (d, $J = 8.4$ Hz, 1H), 4.56–4.50 (m, 2H), 1.38–1.34 (m, 12H).

2-(4-tert-Butyl-phenyl)-1-ethyl-4,7-di-thiophen-2-yl-1H-benzoimidazole (4). To a solution of 4,7-Dibromo-2-(4-tert-butyl-phenyl)-1-ethyl-1H-benzoimidazole (2.97 g, 6.8 mmol) and tributyl(2-thienyl)stannane (5.6 g, 15 mmol) in Toluene (50 mL), $PdCl_2(PPh_3)_2$ (0.28 g, 5 mol%) was added. The mixture was refluxed under a nitrogen atmosphere for 12 h. After cooling the mixture to room temperature, a portion of 100 mL of water was added and the mixture was extracted with ethyl acetate. The organic extraction was dried with anhydrous $MgSO_4$ and the solvent was removed by vacuum evaporation. The residue was purified by column chromatography with hexane/dichloromethane (1/1, volume ratio) as eluent, yielding 2-(4-tert-Butyl-phenyl)-1-ethyl-4,7-di-thiophen-2-yl-1H-benzoimidazole as a yellow solid (2.11 g, 70%). MS: [M^+], m/z 604. ^{1}H-NMR (400 MHz, CDCl$_3$, ppm): δ 8.20–8.19 (dd, $J_1 = 1.2$ Hz, $J_2 = 3.6$ Hz, 1H), 7.69–7.67 (d, $J = 8.3$ Hz, 2H), 7.60–7.58 (d, 7.9 Hz, 1H), 7.53–7.51 (d, $J = 8.6$ Hz, 2H), 7.42–7.41 (dd, $J_1 = 1.2$ Hz, $J_2 = 5.2$ Hz, 1H), 7.36–7.34 (dd, $J_1 = 1.2$ Hz, $J_2 = 5.2$ Hz, 1H), 7.26–7.25 (d, $J = 2.8$ Hz, 1H), 7.16–7.12 (m, 3H), 4.16–4.10 (m, 2H), 1.37 (s, 9H), 0.86–0.83 (t, $J = 7.0$ Hz, 3H).

4,7-Bis-(5-bromo-thiophen-2-yl)-2-(4-tert-butyl-phenyl)-1-ethyl-1H-benzoimidazole (5). 2-(4-tert-Butyl-phenyl)-1-ethyl-4,7-di-thiophen-2-yl-1H-benzoimidazole (0.89 g, 2 mmol) was dissolved in DMF under nitrogen atmosphere, and the N-bromosuccinimide (NBS; 1.07 g, 6 mmol) was added in one portion. The reaction mixture was stirred overnight at room temperature and then the mixture was quenched with 50 mL of water and extracted with ethyl acetate. The combined organic extract was with aqueous sodium sulfide (10 wt.%) and concentrated under reduced pressure to afford a crude product that was purified to column chromatography using hexane/dichloromethane (4/1, volume ratio) to get 4,7-Bis-(5-bromo-thiophen-2-yl)-2-(4-tert-butyl-phenyl)-1-ethyl-1H-benzoimidazole as a white solid (0.6g, 50%). MS: [M^+], m/z 604. ^{1}H-NMR (400 MHz, CDCl$_3$, ppm): δ 7.73–7.71 (d, $J = 7.7$ Hz, 1H), 7.62–7.59 (m, 2H), 7.51–7.49 (m, 2H), 7.26–7.24 (d, $J = 7.32$ Hz, 2H), 7.09–7.05 (m, 2H), 6.93–6.92 (d, $J = 3.7$ Hz, 1H), 4.18–4.13 (m, 2H), 1.34 (s, 9H), 0.93–0.90 (t, $J = 7.0$ Hz, 3H).

Synthesis of POFTBT-IMD. 9,9-Dioctylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester (0.1117 g, 0.2 mmol), TBT (0.0623 g/0.136 mmol for IMD10 and 0.0701 g/ 0.153 mmol for IMD5), compound 5 (0.0204 g/0.034 mmol for IMD10 and 0.0102 g/0.017 mmol for IMD5) and Pd(PPh$_3$)$_4$ (0.0115 g, 0.01 mmol) were dissolved in 3 mL of toluene and purged under a nitrogen atmosphere for 10 min. Subsequently, Tetraethylammonium hydroxide 20% in water (0.8 mL) was added into a flask. The reaction mixture was stirred at 65°C for 2 hours. Bromobenzene was added and stirred for 1 hour. After being cooled to room temperature, the reaction mixture was poured into methanol. The solid was filtered and re-dissolved in chloroform. Ammonium hydroxide solution was added and stirred overnight. The organic layer was washed with deionized water twice. Then it was precipitated in a large amount of methanol. The solid was further purified by Soxhlet extractor using methanol and then hexane for 12 h and dried in a vacuum oven at 60°C for 1h. A dark red powder POFTBT was obtained, and the yield was 70%.

Measurement

^{1}H-NMR and ^{13}C-NMR spectra of compounds were recorded with a JEOL JNM ECP-400 spectrometer. UV–Visible (UV–Vis) and photoluminescence (PL) spectra of the polymers were recorded using a JASCO V-530 Spectrophotometer and a HITACHI F-4500, respectively. Cyclic voltammetry (CV) was performed by a CompactStat-Plus (Ivium technology) Scanning Potentiostat with a three electrode cell in a solution of 0.10 M tetrabutylammonium hexafluorophosphate (Bu$_4$NPF$_6$) in freshly distilled MC at a scan rate of 100 mV/s. Pt coil and wire were used as the counter and working electrode and an Ag/Ag$^+$ electrode was used as the reference electrode.

Results and Discussion

Synthesis and Characterization. The chemical structure of 2-(4-tert-Butyl-phenyl)-1-ethyl-4,7-di-thiophen-2-yl-1H-benzoimidazole was confirmed by ^{1}H-NMR spectrum in CDCl$_3$ is shown in Fig. 1.

Table 1. Summary of optical and electrochemical data of polymers

	HOMO (eV)[a]	LUMO (eV)[b]	E_{gap} (eV)[c]	UV_{max} (nm)	PL_{max} (nm)
POFTBT	−5.3	−3.7	1.93	558	665
POFTBT-IMD 5	−5.4	−3.84	1.93	559	653
POFTBT-IMD 10	−5.4	−3.81	1.94	555	659

[a] Estimated from the LUMO energy level and band gap energy.
[b] Figured out from the reduction onset potential.
[c] Estimated from the absorption edge of UV-Vis spectrum.

As shown Fig. 2, three polymers POFTBT, POFTBT-IMD5 and POFTBT-IMD10 were synthesized and characterized by the FT-IR spectra. For POFTBT-IMD5 and POFTBT-IMD10, we can observe C-N stretching vibration in imidazole appears around 1440–1460 cm^{-1}. However, POFTBT does not shows C-N stretching vibration. Polymers were good soluble in common organic solvents such as THF, toluene, chloroform and *o*-dichlorobenzene.

Optical and Electrochemical Properties. The photo-physical characteristics of the polymers were investigated by UV-Vis absorption spectrophotometry. Figure 3 shows the absorption spectra of POFTBT, POFTBT-IMD5 and POFTBT-IMD10. All of the polymers have absorption around 360–420 nm which we assign to localized π–π^* transition bands, and the other broad absorption signals around 540 $\sim$ 580 nm which were attributed to internal charge transfer (ICT) interactions between the TBT, IMD acceptor moieties and 9,9-dioctylfluorene donor units. The absorption band of three polymers located at 558, 559, 555 nm and optical band gaps estimated from the absorption edge in the UV-Vis spectrum of the thin solid film are 1.93, 1.93 and 1.94 for POFTBT, POFTBT-IMD5 and POFTBT-IMD10, respectively.

The information about energy levels of π-conjugated polymer is very important to determine the open circuit voltage (V_{oc}) and the charge separation of organic solar cells (OSCs). Cyclic voltammetry (see Fig. 4) was used to estimate the HOMO and LUMO energy levels of polymers. Polymers underwent quasi-reversible p-doping and irreversible n-doping

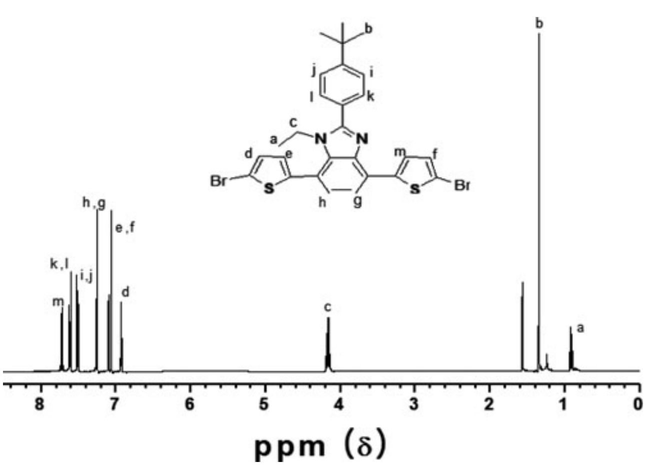


Figure 1. 1H-NMR spectrum and chemical structure of monomer in $CDCl_3$ solution.

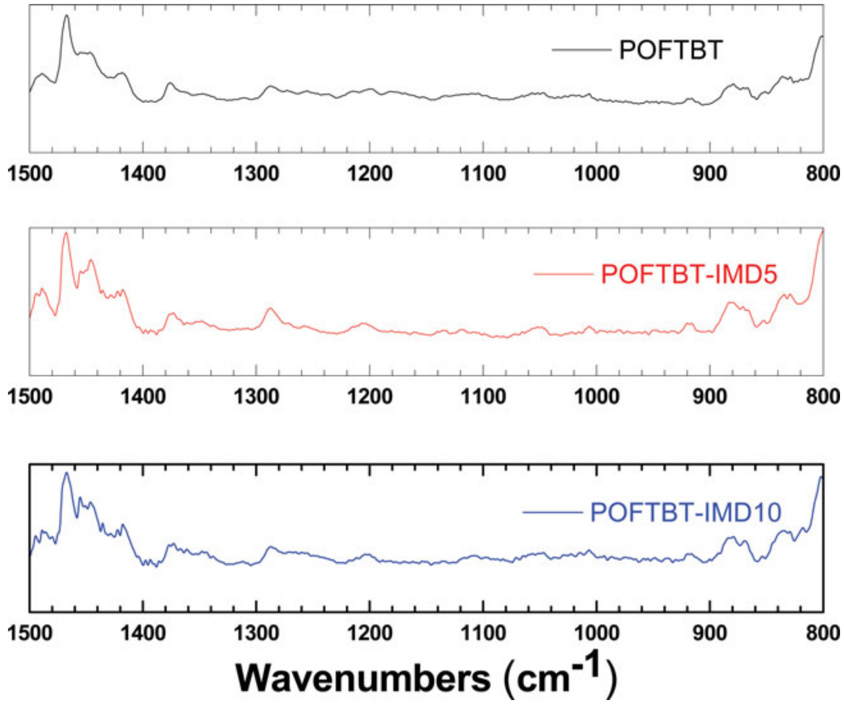


Figure 2. FT-IR spectrum of polymers.

process in the positive and negative scans. The energy levels of polymers were calculated from the onset potential of oxidation by assuming the energy level of ferroccene (Fc) as −4.8 eV. The LUMO energy level of POFTBT, POFTBT-IMD5 and POFTBT-IMD10 figured out from the reduction onset potential were −3.7, −3.84, −3.81 eV, respectively. The HOMO energy level of POFTBT, POFTBT-IMD5 and POFTBT-IMD10 were −5.3, −5.4, −5.4 eV, respectively. The optical and electrochemical properties are summarized in Table 1.

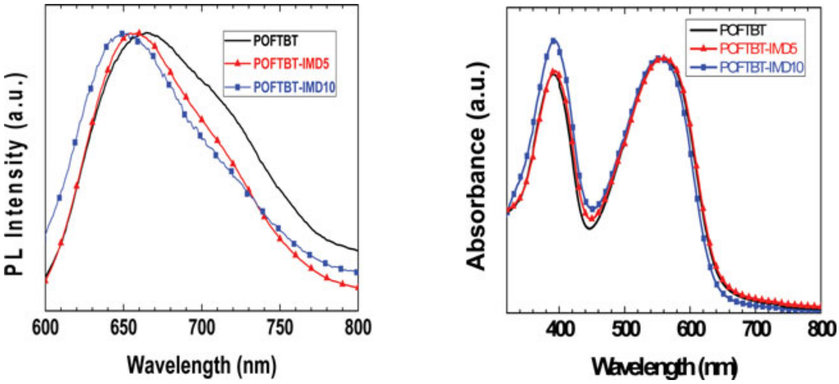


Figure 3. Normalized UV-Vis absorption and photoluminescence spectrum of polymers.

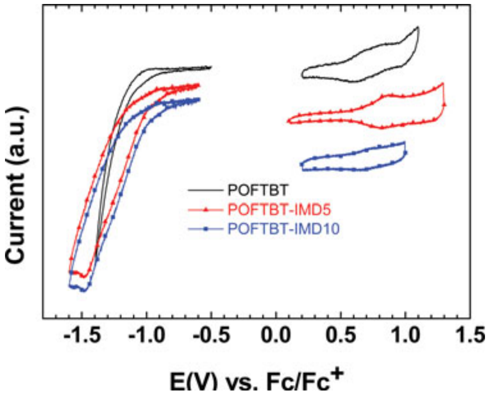


Figure 4. Cyclic voltammogram of polymers.

Conclusions

We synthesized copolymers with 9,9-dialkylflourence, 4,7-di-thiophen-2-yl-4,5,6,7-tetrahydro-benzo [1,2,5] thiadiazole (TBT) and 2-(4-tert-Butyl-phenyl)-1-ethyl-4,7-di-thiophen-2-yl-1H-benzoimidazole (IMD) through the Suzuki coupling reaction. A new π-conjugated polymer with IMD, PFTBT-IMD, showed similar optical and electrochemical properties with those of π-conjugated polymer without IMD.

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