



Synthesis and Properties of New Low Band Gap Semiconducting Polymers

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Low band gap organic semiconducting polymers were prepared as *p*-type donors for organic photovoltaic devices. A novel dibrominated monomer composed of phenothiazine, thiophene, and benzothiadiazole (DPDTBT) was synthesized as a low band gap core block. DPDTBT was copolymerized with three different boronic esters of dithiophene, fluorene, and phenothiazine by the Suzuki coupling polycondensation reaction. The band gap energies of the synthesized polymers ranged between 2.05 and 2.11 eV, depending on the polymer structure. Bulk heterojunction solar cells fabricated using the polymers and [6,6]-phenyl C_{71} -butyric acid methyl ester (PC₇₀BM) as an acceptor were characterized. The best power conversion efficiency obtained from the fabricated devices under simulated AM 1.5 G solar irradiation of 100 mW/cm² was 0.46%.

Keywords: Low Band Gap, Organic Semiconducting Polymer, Solar Cell.

1. INTRODUCTION

In the last few decades, organic semiconducting materials have attracted considerable attention in science and technology for use in diverse applications such as transistors, photovoltaic devices, and polymer light-emitting diodes (PLEDs). This wide range of applicability of PLED is due to their excellent electrical and optical properties and good processibility comparable to that of inorganic semiconductors.¹⁻³ Recently, organic photovoltaic (OPV) cells fabricated using conjugated polymer and soluble fullerene derivative composites have attracted much attention because of their numerous advantages such as low production cost and ease of manufacture by solution processes.⁴⁻⁷ However, the power conversion efficiencies (PCEs) of the polymer PV cells are lower than those of silicon based solar cells. To improve the PCE of polymer PV cells, efforts should be made to achieve efficient light harvesting by the photoactive layer, and enhanced

interface contact between the metal electrode and the photoactive layer, and improved charge carrier mobility. For application in bulk heterojunction OPVs, conjugated polymers should have good solubility which would facilitate solution-processing and film-forming, show a strong and broad absorption band in the visible near-IR region to enable efficient sunlight harvesting, and have high charge carrier mobility and purity.

Recently, we designed a new low band gap monomer unit composed of phenothiazine, thiophene, and benzothiadiazole (DPDTBT). 4,7-Bis(5-bromothiophene-2-yl) benzo[c][1,2,5]thiadiazole was coupled with two phenothiazine boronic esters by the Suzuki coupling reaction. Phenothiazine is a well-known electro-active heterocyclic compound with electron-rich sulfur and nitrogen heteroatoms. Molecules and polymers containing phenothiazine moieties have recently attracted much research interest.^{8–10} We expected that conjugation of phenothiazine with the electron-withdrawing benzothiadiazole moiety would result in improved hole mobility and a narrow

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Scheme 1. Synthetic route of low band gap polymers. 61.111 On: 11

band gap. DPDTBT was copolymerized with three counter boronic ester monomers of dithiophene, fluorene and phenothiazine by the Suzuki coupling polycondensation reaction to give PBTPTBT, PFPTBT and PPPTBT, respectively. Depending on their structure, the synthesized polymers showed band gap energies between 2.05 and 2.11 eV. Photovoltaic devices were fabricated using the polymers and characterized. The synthetic route and polymer structures are shown in Scheme 1.

2. EXPERIMENTAL DETAILS

2.1. Materials

Tetrakis(triphenylphosphine)-palladium, potassium carbonate, and bromine (Br₂) were purchased from Aldrich and used without further purification. All the solvents were dried and purified under nitrogen. 4,7-Bis(5-bromothiophen-2-yl)benzo[c][1,2,5]thiadiazole11 and 10-(2-ethylhexyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-10H-phenothiazine12 were synthesized according to the reported methods.

2.2. Measurements

¹H and ¹³C NMR spectra were recorded using a Bruker AM-400 spectrometer. UV-vis and photoluminescence (PL) spectra were recorded using a Shimadzu UV-3600 spectrophotometer, and a Shimadzu RF-5301PC fluorometer, respectively. Thermo-gravimetric analysis (TGA) was carried out using a Q500 analyzer at a heating rate of 10 °C/min in a nitrogen atmosphere. The polymer molecular weights were determined by gel permeation chromatography (GPV) using a GPCV 2000 instrument, with THF as the eluent and polystyrene as the standard. Cyclic voltammetry (CV) measurements were performed using an AUTOLAB potentiostat/galvanostat at room temperature with a three-electrode cell in a solution of TBABF4 (0.10 M) in acetonitrile at a scan rate of 50 mV/s.

2.3. Fabrication of Polymer Solar Cells

Polymer solar cells with the structure ITO/PEDOT:PSS/ Polymers:PC₇₀BM (1:5, w/w)/TiO_r/A1 (120 nm) were fabricated as follows. A 40-nm-thick layer of poly(3,4ethylenedioxythiophene):poly(styrenesulfonate) was spincoated onto a precleaned, indium tin oxide (ITO)-coated glass substrate. This was followed by spin coating of the polymer/PC70BM blend solution on to the substrate. The concentration of the polymer:PC70BM blend solution used for spin coating was 10 mg/mL, and dichlorobenzene and CHCl₃ were used as the solvents. The thickness of the active layer was ~ 80 nm. Then, the TiO_x precursor solution was spin-cast in air on top of the polymer:PC70BM composite layer. Subsequent heating of the composite for 10 min at 80 °C in air resulted in hydrolysis of the precursor and conversion to TiO_x . Finally, the device fabrication was completed by deposition of Al metal electrodes by evaporation. The devices were illuminated using a solar simulator (Oriel 300 W) equipped with an air mass (AM) 1.5 G filter at a power of 100 mW/cm². The current density-voltage (J-V) characteristics were recorded with a Keithley 236 source meter.

2.4. Synthesis of Monomers and Polymers

4,7-Bis (5-bromothiophen-2-yl) benzo [*c*][1,2,5] thiadiazole (1). 4,7-Di(thiophen-2-yl)benzo[*c*][1,2,5] thiadiazole (4.0 g, 13.3 mmol) was dissolved in CHCl₃ (100 mL) and a catalytic amount of acetic acid. Then, N-bromosuccinimide (NBS) (5.5 g, 30.6 mmol) was added portion wise, and the mixture was stirred for 36 h at room temperature with light protection. The precipitate was filtered through a Büchner funnel, and then washed with copious amounts of MeOH, water, and acetone. The product was collected as a red solid (4.6 g, 76%). ¹H NMR (400 MHz, CDCl₃): δ 7.80 (dd, 4 H), 7.13 (*d*, 2 H). ¹³C NMR (400 MHz, CDCl₃): δ 154.2, 140.8, 131.1, 129.6, 129.1, 128.0, 111.6.

3-(4,4,5,5-Tetramethyl-1,3,2-di-oxaborolan-2-yl)-10-(2ethylhexyl)-phenothiazine (2). 3-Bromo-10-(2-ethylhexyl)phenothiazine (3.0 g, 7.7 mmol) was dissolved in THF (150 mL) at -78 °C. To the solution, 4.6 ml of *n*-butyllithium (2.0 M in pentane) was added by a syringe. The mixture was stirred at -78 °C for 2 h. 2-Isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3.1 mL) was

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added to the solution, and the resulting mixture was stirred at -78 °C for 1 h, warmed to room temperature, and stirred for 40 h. The mixture was poured into water, extracted with dichloromethane, and dried over MgSO₄. The solvent was removed by evaporation, and the residue was purified by column chromatography using ethylac-etate/hexane (1:9) as the eluent. The product was collected as a green liquid. (2.7 g, 79%). ¹H NMR (400 MHz, CDCl₃): δ 7.50 (*m*, 4 H), 6.91 (*d*, 1 H), 6.58–6.55 (*m*, 2 H), 3.80 (*d*, 2 H), 1.75 (*m*, 1 H), 1.32 (*s*, 12 H), 1.48–1.20 (*m*, 8 H), 0.85 (*m*, 6 H). ¹³C NMR (400 MHz, CDCl₃): δ 145.1, 138.2, 133.2, 132.8, 130.1, 129.5, 127.1, 123.2, 122.5, 120.1, 118.2, 115.0, 88.3, 68.1, 38.5, 33.2, 30.2, 26.9, 24.7, 23.5, 15.2, 12.1.

Synthesis of 4,7-bis(5-(7-bromo-10-(2-ethylhexyl)-10 H-pheno-thiazin-3-yl)thiophen-2 yl)benzo[c][1,2,5]thiadiazole (DPDTBT). To a 100-mL two-neck flask were added 1.0 g (2.2 mmol) of 1 and 2.0 g (4.6 mmol) of 2 in 20 mL of anhydrous toluene. Tetrakis(triphenylphosphine) palladium (0.076 g, 0.07 mmol) was transferred to the mixture in an inert atmosphere. Aqueous potassium carbonate (2.0 M) and several drops of Aliquat336 in toluene were transferred to the reaction mixture via a cannula. The reaction mixture was stirred at 80 °C for 24 h. The obtained product was further reacted with two equivalents of Br₂ in dichloromethane for 2 h at room temperature. The resulting mixture was extracted with CHCl₃ and dried over MgSO₄. The solvent was removed by evaporation, and the residue was purified by column chromatography. The product was obtained as a red solid. (1.0 g, 52%). 1 H NMR (400 MHz, CDCl₃): δ 8.23 (d, 2 H), 8.18 (q, 4 H), 8.03 (d, 2 H), 7.97 (m, 2 H), 7.69 (m, 2 H), 7.57 (t, 2 H), 7.39 (t, 2 H), 7.17 (s, 2 H), 4.20 (2, 4 H) 2.07 (m, 2 H), 1.42 (m, 16 H), 0.89 (m, 12 H). ¹³C NMR (400 MHz, CDCl₃): δ 155.3, 148.6, 145.3, 139.7, 138.1, 129.9, 128.7, 128.1, 127.5, 126.4, 125.9, 125.5, 125.1, 125.0, 124.9, 124.1, 123.1, 122.8, 115.7, 49.52, 30.0, 20.3, 13.8. Calcd for C₄₆H₃₆Br₂N₂S₅: C, 57.26; H, 3.76; N, 5.81; S, 16.62. Found: C, 56.96; H, 3.72; N, 5.75; S, 15.54.

Synthesis of PBTPTBT, PFPTBT and PPPTBT. PBTPTBT, PFPTBT and PPPTBT were prepared via similar procedures by coupling DPDTBT with the three corresponding boronic esters. DPDTBT (1.0 mmol), the boronic ester (1.0 mmol), and toluene (20 mL) were placed in a two-necked flask. The solution was flushed with argon for 10 min, and then, 23 mg of Pd(PPh₃)₄ was added into the flask. The solution was flushed again for 20 min. The oil-bath temperature was raised to 110 °C, and the reaction was stirred for 48 h in an argon atmosphere. Then, the reaction mixture was cooled to room temperature, and the product was precipitated by adding the reaction mixture to 300 mL of MeOH. The resulting polymers were purified by successive extractions with methanol, hexane, and acetone using a Soxhlet extractor. The polymer yields were 52%, 36% and 20% for PBTPTBT, PFPTBT, and PPPTBT, respectively.

3. RESULTS AND DISCUSSION

3.1. Characterization of the Polymers

All the synthesized polymers were completely soluble in common organic solvents such as THF and CHCl₃. The polymer solutions were spin-coated onto glass or ITO substrates to form transparent, homogeneous thin films. The number-average molecular weights (M_n) of the polymers as determined by GPC using a polystyrene standard, were found to range from 7,700 to 15,100, with polydispersity indices ranging from 2.3 to 2.9. The thermal properties of the polymers were determined by TGA. All the polymers were found to exhibit good thermal stability, with weight loss of less than 5% upon heating to temperature above 320 °C. The molecular weights and decomposition temperatures of the polymers are summarized in Table I.

3.2. Optical and Electrochemical Properties

The optical properties of the polymers were investigated using UV-visible absorption spectroscopy. Spectra were obtained in solution and thin-film states. Figure 1 shows the absorption spectra of the polymer solutions in CHCl₃. The polymers exhibited two absorption peaks at approximately 350 and 460 nm, which is a common feature of internal donor/acceptor polymers. PBTPTBT exhibited absorption at a longer wavelength than did other the polymers. In the spectra of the polymer films, the absorption peaks shifted to longer wavelength, and the absorption intensity increased in the region where the wavelength exceeded 600 nm as shown in Figure 2. The absorption peaks in the spectra of the polymer films at short wavelengths (347–363 nm) originated from the π - π * transitions of electron donor units, while the absorption peaks at longer wavelengths (466–469 nm) are due to the π – π * transitions of the benzothiadiazole moiety.

Electrochemical CV has been widely employed to investigate the redox behavior of polymers and to estimate their HOMO and LUMO energy levels. In this study, CV was performed in solutions of Bu_4NBF_4 (0.10 M) in dichloromethane at a scan rate of 100 mV/s, at room temperature in an argon atmosphere.

A platinum plate, a platinum wire, and a $Ag/AgNO_3$ electrode were used as the working electrode, counter electrode, and reference electrode, respectively. The HOMO energy level was calculated using E_{ox} . The LUMO energy levels of the polymers were estimated from the onset of the absorption peak in the spectra of the copolymer films.

Table I. Molecular weights and thermal properties of the polymers.

Polymers	M_n^a	M^a_w	PDI ^a	T^b_d (°C)
PBTPTBT	15,100	37,300	2.47	327.1
PFPTBT	9,400	25,900	2.76	341.8
PPPTBT	7,700	17,600	2.29	349.4

Notes: ^{*a*}Mn, Mw, and PDI of the polymers were determined by gel permeation chromatography using polystyrene standards in CHCl₃; ^{*b*}Temperature at 5% weight loss by a heating rate of 10 °C/min under nitrogen.

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Figure 1. UV-vis absorption spectra of polymers in chloroform solution.

To obtain accurate redox potentials, the reference electrode was calibrated against the ferrocene/ferrocenium (Fc/Fc⁺) redox couple, the redox potential of which is assumed to have an absolute energy level of -4.80 eV in vacuum. Thus, the HOMO energy values were calculated using the equation $E_{\text{HOMO}} = (E_{\text{onset, ox.}} + 4.4) \text{ eV}$, where E_{ox} is the onset oxidation potential versus Ag/Ag⁺. The HOMO energy levels obtained for PBTPTBT, PFPTBT, and PPPTBT were -5.30, -5.34, and -5.33 eV, respectively. The absorption properties, HOMO and LUMO energy levels, and band gap energies of the polymers are listed in Table II and Figure 3.

3.3. Photovoltaic Properties

Bulk heterojunction polymer solar cells were fabricated with the structure ITO/PEDOT:PSS (40 nm)/ polymer:PC70BM(1:5, w/w) (80 nm)/TiO_x (20 nm)/Al (120 nm) where the polymers were used as electron donors and PC₇₀BM as an electron acceptor. Figure 4 shows the J-V curves of the devices. The devices comprising PFPTBT and PPPTBT showed high open-circuit voltages



Figure 2. UV-visible absorption spectra of polymers solid films.

Summary of photophysical and electrochemical properties of

polymers.									
	$\lambda_{\max, abs}$ (nm)								
Polymers	Sol. ^a	Film ^b	HOMO (eV)	LUMO (eV)	$E_g^{\text{opt}} \ (\text{eV})^c$				
PBTPTBT	357	363	-5.30	-3.23	2.07				
PFPTBT	351	354	-5.45	-3.34	2.11				
PPPTBT	324	347	-5.33	-3.28	2.05				

Table II.

Notes: ${}^{a}1 \times 10^{-5}$ M in anhydrous chloroform; b Polymer film on a quartz plate by spin-casting from a solution in chloroform at 1500 rpm for 30 s; c Calculated from the absorption band edge of the copolymer films, $E_{g} = 1240/\lambda_{edge}$.



Figure 3. Energy band diagram for the devices.

(> 0.6 V), but the PCE were low because of their low short-circuit current densities.

The device fabricated using PBTPTBT produced the best results among the devices fabricated in this study. The open-circuit voltage, short-circuit current density, and fill factor of the device were 0.56 V, 2.79 mA/cm², and 0.30, respectively. The calculated PCE of the device containing PBTPTBT was 0.46%. The solar cells fabricated using the synthesized polymers showed relatively high open-circuit



Figure 4. J-V characteristics of the fabricated solar cells.

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Table III. Summary of performances of the fabricated solar cells.								
Active layer	$J_{\rm sc}^a~({\rm mA/cm^2})$	$V^a_{ m oc}$ (V)	FF^{a} (%)	PCE^{a} (%)				
PBTPTBT:PC70BM	2.79	0.56	0.30	0.46				
PFPTBT:PC70BM	0.82	0.60	0.26	0.13				
PPPTBT:PC ₇₀ BM	1.54	0.61	0.31	0.29				

Notes: ^aPhotovoltaic properties of copolymers/PCBM-based devices spin-coated from a dichlorobenzene solution for polymers (1:5 w/w).

voltages but low short-circuit current densities. The device performances are summarized in Table III. Further optimization of these devices, by modification of the thickness parameters and annealing conditions is currently under investigation.

4. CONCLUSIONS

Three new low band-gap organic semiconducting polymers were synthesized as *p*-type donor materials for organic photovoltaic devices. The synthesized polymers had number-average molecular weights between 7,700 and 15,100. The band-gap energies of the synthesized polymers ranged between 2.05 and 2.11 eV depending on the polymer structure.

Bulk-heterojunction solar cells fabricated using the polymers and $PC_{70}BM$ as an acceptor were characterized. One of the devices showed a PCE of 0.46% under simulated AM 1.5 G solar irradiation of 100 mW/cm². Ingenta to:

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