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Low bandgap polymers with benzo [1,2-b:4,5-b′] dithiophene and bisthiophene-dioxopyrrolothiophene units for photovoltaic applications

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ABSTRACT

New donor/acceptor polymers **PBDTTPT1** and **PBDTTPT2** with alternating benzodithiophene (BDT) and bisthiophene-dioxopyrrolothiophene (TPT) units were synthesized by Stille coupling reaction. The polymers had optical bandgaps of 1.78 and 1.82 eV, and HOMO energy levels of −5.30 and −5.35 eV for **PBDTTPT1** and **PBDTTPT2**, respectively. Polymeric solar cell devices based on these copolymers as donors and $PC_{71}BM$ as acceptor showed the highest open circuit voltage of 0.95 V and power conversion efficiency of 2.68% under the illumination of AM 1.5, 100 mW/cm^2.

1. Introduction

Research on polymeric solar cells (PSCs) has been intensified in recent years because PSCs have a potential to generate electricity from sunlight at low cost [1–8]. Bulk heterojunction (BHJ) structure based on blending of electron-donating conjugated polymers and high-electron-affinity fullerene derivatives such as PCBM has become the most successful device structure for organic photovoltaics (OPVs) [9,10]. So far, the power conversion efficiency (PCE) of PSCs is still low in comparison with the silicon based solar cells. Four steps are involved the organic photovoltaic phenomena. They are photon absorption and generation of exciton, exciton diffusion, exciton separation and separated charge carriers migrate to electrodes. Short circuit current (J_{sc}), open circuit voltage (V_{oc}) and fill factor (FF) are three main parameters that determine the PCE of the PSC devices. Many examples of low bandgap polymers, absorbing in the red and near-IR regions of the solar spectrum, have been developed for maximizing solar photon harvest, thereby increasing J_{sc} and PCE [11–14]. Systematic studies on matching the energy levels of donor polymers with those of PCBM have been carried out [15,16]. Low bandgap polymers with deep HOMO energy level will result high J_{sc} and V_{oc} simultaneously, thereby maximizing power conversion efficiency.

Recently, low bandgap polymers with deep HOMO energy level have been studied for achieving high V_{oc} in PSC devices [17–20]. Polymers containing dioxopyrrolothiophene (**DPT**) unit have achieved the V_{oc} of about 0.9 V and PCE around 4–7% [21–25]. In our previous work, two polymers (**PBDTDPTs**) based on benzo [1,2-b:4,5-b′] dithiophene (**BDT**) and **DPT** units were synthesized and were shown relatively high performance in solar cell devices [25]. However, **PBDTDPT** polymer films have absorption spectra edged around 675 nm. Design and synthesis of new polymers with substantial absorption in longer wavelength will have lower bandgap and may result better solar photon harvest. Recently, there are reports on further reduction of polymer bandgaps by incorporation of additional electron-rich thiophene moieties into existing donor/acceptor polymers [26–28]. Herein, we report the synthesis and structure/property relationship on two new low bandgap polymers based on **BDT** and **DPT** units with additional alkyl-substituted thiophene moieties.

2. Experimental section

2.1. Materials

n-Butyllithium, trimethyltin chloride and triphenylarsine were obtained from Alfa Aesar Chemical Company. Tris (dibenzylideneacetone) dipalladium (Pd_2dba_3) and *tri-o*-tolylphosphine were purchased from Sigma–Aldrich Chemical Company. All materials were used as

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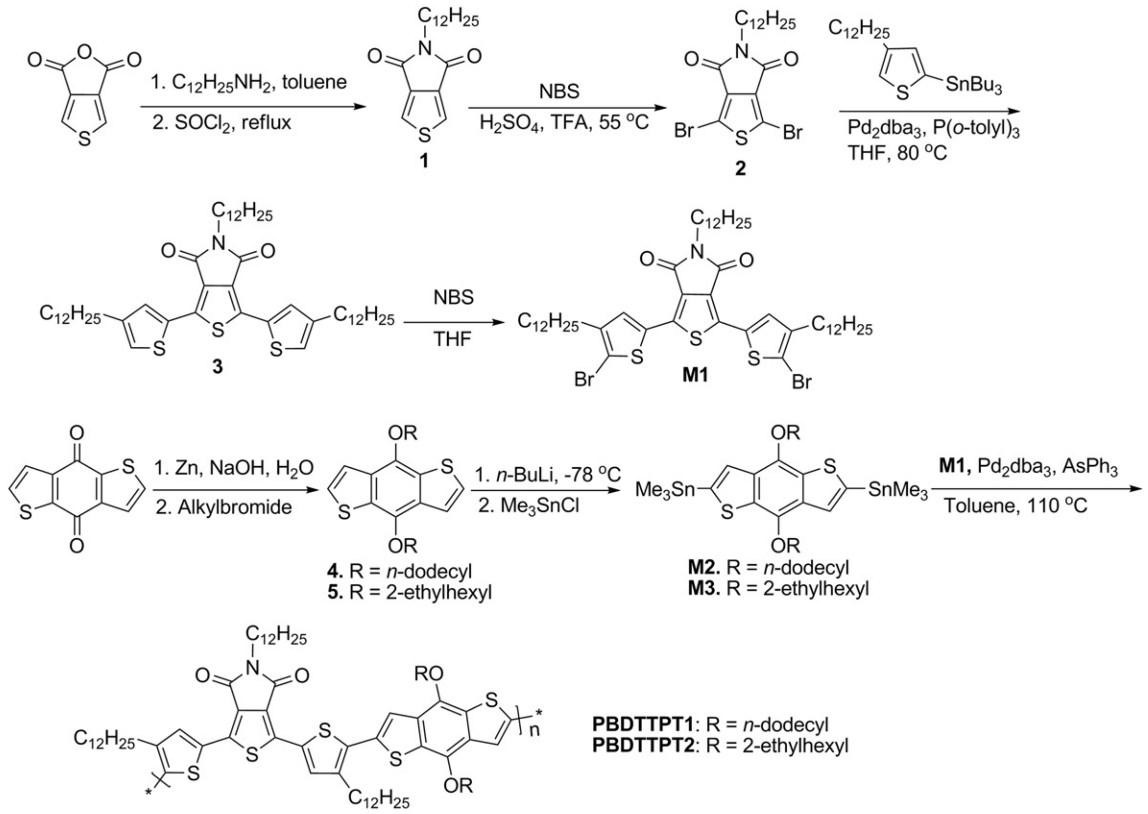

Scheme 1. Synthesis of monomers and polymer **PBDTTPT1** and **BDTTPT2**.

received without further purification. Tetrahydrofuran (THF) and toluene were freshly distilled over Na wire under nitrogen prior to use.

2.2. Measurements and characterization

Nuclear Magnetic Resonance spectra were recorded on a Mercury plus 400 MHz machine. Gel permeation chromatography (GPC) analyses were performed on a Perkin Elmer Series 200 gel coupled with UV–vis detector using tetrahydrofuran as eluent with polystyrene as standards. Thermogravimetric analysis (TGA) analyses were conducted with a TA instrument QS000IR at a heating rate of 20 °C min^{-1} under nitrogen gas flow. Differential scanning calorimetry (DSC) analysis was performed on a TA instrumentation Q2000 in a nitrogen atmosphere. All the samples (about 10.0 mg in weight) were first heated up to 300 °C and held for 2 min to remove thermal history, followed by the cooling rate of 20 °C/min to 20 °C and then heating rate of 20 °C/min to 300 °C in all cases. UV–vis absorption spectra were recorded on a Perkin Elmer model λ 20 UV–vis spectrophotometer. Electrochemical measurements were conducted with a CHI 600 electrochemical analyzer under nitrogen in a deoxygenated anhydrous acetonitrile solution of tetra-*n*-butylammonium hexafluorophosphate (0.1 M). A platinum electrode was used as a working electrode, a platinum-wire was used as an auxiliary electrode, and an Ag/Ag^{+} electrode was used as a reference electrode. Polymer thin films were coated on platinum electrode and ferrocene was added as reference. A potential scan rate of 100 mV/s was used for all experiments.

2.3. Device fabrication and characterization of solar cells

Polymer solar cells (PSCs) with the device structures of ITO/PEDOT: PSS/polymer: $PC_{70}BM$ (1:2, w/w)/LiF/Al were fabricated as follows: a ca. 40-nm-thick PEDOT: PSS (Baytron P AI 4083) was spin-coated from an aqueous solution onto the pre-cleaned ITO substrates, and dried at 120 °C for 30 min in air. Then the substrates were transferred into a nitrogen filled glove box. The prepared solution of **PBDTTPT**: $PC_{70}BM$ (5 mg/mL: 10 mg/mL) in chloroform with or without diiodooctane (2 vol%) was spin-coated on top of the PEDOT/PSS layer. Finally the samples were transferred into an evaporator and LiF (1 nm) and Al (100 nm) with area of 0.12 cm^2 were thermally deposited under a vacuum of 10^{-6} Torr. The devices were encapsulated in a glove box and measured in air. Current-voltage characteristics were measured using a computer controlled Keithley 236 source meter. The photocurrent was measured under AM 1.5G illumination at 100 mW/cm^2 from a solar simulator (Oriel, 91160A-1000). The external quantum efficiency (EQE) was measured at a chopping frequency of 280 Hz with a lock-in amplifier (Stanford, SR830) during illumination with the monochromatic light from a Xenon lamp.

2.4. Synthetic procedures

4,8-Dihydrobenzoldithiophene-4,8-dione [29], thiophene-3,4-dicarboxylic anhydride [30] and 5-tri-*n*-butylstannyl-3-dodecylthiophene [31] were synthesized according to the literature. The synthesis of monomer **M1**, **M2**, **M3** and the polymers are showed in Scheme 1.

2.4.1. 5-Dodecylthieno [3,4] pyrrole-4,6-dione (*1*)

A solution of thiophene-3,4-dicarboxylic anhydride (3.09 g, 20.05 mmol) and *n*-dodecylamine (4.09 g, 22.06 mmol) in toluene (250 mL) was refluxed for 24 h in a flask. After cooled to room temperature, the reaction mixture was filtrated and was dried under vacuum to afford a brown solid. Thionyl chloride (200 mL) was added and the mixture was refluxed for 5 h. The volatile was removed under vacuum. The residue was recrystallization from hexane to afford the titled compound as white crystals (3.25 g, 50.5%). ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.82 (s, 2H), 3.60 (t, $J = 4.0$ Hz, 2H), 1.63 (m, 2H), 1.25 (m, 18H), 0.87 (t, $J = 6.8$ Hz, 3H).

2.4.2. *1,3-Dibromo-5-dodecylthieno [3,4] pyrrol-4,6-dione (**2**)*

N-Bromosuccinimide (NBS) (6.65 g, 37.33 mmol) was added to the solution of compound **1** (3.0 g, 9.33 mmol), concentrated sulfuric acid (12.0 mL) and trifluoroacetic acid (40 mL). The reaction mixture was stirred at 55 °C for 24 h. The brown solution was poured into ice water (500 mL) and was extracted with dichloromethane. The organic layer was collected and was dried with anhydrous sodium sulfate. Solvent was removed under reduced pressure and residue was purified by flash chromatography on silica gel with diethyl ether/dichloromethane/petroleum ether (1: 1: 15) as eluent to give the titled compound (2.79 g, 62.5%). ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) 3.58 (t, $J = 7.2$, 2H), 1.62 (m, 2H), 1.25 (m, 18H), 0.87 (t, $J = 6.8$ Hz, 3H). ^{13}C (100 MHz, $CDCl_3$), δ (ppm): 160.58, 135.00, 113.13, 39.05, 32.14, 29.86, 29.80, 29.67, 29.57 (2C), 29.38, 28.48, 27.02, 22.92, 14.37.

2.4.3. *1,3-Bis(4-n-dodecylthiophene)-5-dodecylthieno [3,4] pyrrol-4,6-dione (**3**)*

5-Tri-n-butylstannyl-3-dodecylthiophene (5.64 g, 10.43 mmol) and compound **2** (2.0 g, 4.17 mmol) were dissolved in tetrahydrofuran (20 mL) in a pressure tube. The solution was degassed by a nitrogen flow for 30 min. Then Pd_2dba_3 (0.076 g, 0.0834 mmol) and tri-*o*-tolylphosphine (0.051 g, 0.167 mmol) were added into the solution. The tube was capped and heated to 80 °C for 36 h. After cooled to room temperature, the mixture was poured into an aqueous solution of potassium fluoride (100 mL, 1.0 M) and stirred for 30 min. The mixture was extracted with dichloromethane (3x). The combined organic layer was dried over anhydrous sodium sulfate. After removing solvent, the residue was purified by column chromatography on silica gel using petroleum ether/dichloromethane (30: 1) as eluent. A yellow solid was obtained after removal of the solvent (2.2 g, 64.3%). ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.87 (s, 2H), 7.02 (s, 2H), 3.65 (t, $J = 7.6$ Hz, 2H), 2.62 (t, $J = 7.6$ Hz, 4H), 1.65 (m, 6H), 1.23–1.35 (m, 54H), 0.88 (t, $J = 6$ Hz, 9H). ^{13}C (100 MHz, $CDCl_3$), δ (ppm): 162.88, 145.14, 136.97, 132.35, 131.28, 128.23, 123.72, 38.80, 32.16, 30.68, 30.64, 29.92, 29.90, 29.85, 29.82, 29.60, 29.58, 29.54, 29.50, 28.78, 27.24, 22.93, 14.37.

2.4.4. *1,3-Bis(4-n-dodecyl-5-bromo-thiophene)-5-dodecylthieno [3,4] pyrrol-4,6-dione (**M1**)*

Compound **3** (1.66 g, 2.02 mmol) and tetrahydrofuran (80 mL) were added into a flask (250 mL) wrapped with aluminum foil. The solution was stirred and degassed for 30 min. *N*-Bromosuccinimide (NBS) (0.79 g, 4.45 mmol) was added in portions over a period of 30 min. The mixture was stirred at room temperature for 2 h, and then the solution was poured into water (100 mL) and was extracted with diethyl ether. The combined organic layer was dried with anhydrous sodium sulfate. Solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel with petroleum ether/dichloromethane (30: 1) as eluent. After removing solvent, a yellow solid (1.28 g, 65.3%) was obtained. ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.63 (s, 2H), 3.64 (t, $J = 7.6$ Hz, 2H), 2.57 (t, $J = 7.6$ Hz, 4H), 1.62 (m, 6H), 1.20–1.35 (m, 54H), 0.87 (t, $J = 6.4$ Hz, 9H). ^{13}C (100 MHz, $CDCl_3$), δ (ppm): 162.64, 143.94, 135.66, 132.05, 130.45, 128.47, 113.76, 38.90, 32.18, 32.16, 29.92, 29.89, 29.82, 29.75, 29.74, 29.62, 29.48, 29.61, 28.74, 27.22, 22.95, 14.38.

2.4.5. *4,8-Didodecyloxybenzo [1,2-b:4,5-b′] dithiophene (**4**)*

Water (40 mL) was added to benzo [1,2-b:4,5-b′] dithiophene-4,8-dione (2.20 g, 10.0 mmol), zinc power (1.96 g, 30.0 mmol) and sodium hydroxide (8.00 g, 200.0 mmol) in a round bottom flask (150 mL). After refluxing for 1 h, a catalytic amount of tetra-*n*-butylammonium bromide (0.032 g, 0.1 mmol) was added. 1-Bromodedecane (7.50 g, 30 mmol) was added drop-wise to the flask. The reaction was refluxed overnight. After cooled to room temperature, it was poured into water (200 mL). The mixture was extracted with diethyl ether for three times. The combined organic layer was dried with anhydrous sodium sulfate. Solvent was removed under reduced pressure and residue was purified by flash chromatography on silica gel with dichloromethane/hexane (1: 15) as eluent to give the titled compound as white solid (3.61 g, 64.7%). ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.48 (d, $J = 5.2$ Hz, 2H), 7.36 (d, $J = 5.2$ Hz, 2H), 4.27 (t, $J = 6.4$ Hz, 4H), 1.86–1.92 (m, 4H), 1.54 (m, 4H), 1.23–1.37 (m, 32H), 0.88 (t, $J = 6.4$ Hz, 6H).

2.4.6. *4,8-Di(2-ethylhexyloxy)benzo [1,2-b:4,5-b′] dithiophene (**5**)*

Same procedure was used as for compound **4**. Compound used were benzo [1,2-b:4,5-b′] dithiophene-4,8-dione (2.20 g, 10.0 mmol), zinc power (1.96 g, 30.0 mmol), sodium hydroxide (8.00 g, 200.0 mmol), 1-bromo-2-ethylhexane (5.79 g, 30.0 mmol) and a catalytic amount of tetra-*n*-butylammonium bromide (0.032 g, 0.1 mmol). A light yellow oil was obtained (2.61 g, 58.2%). ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.49 (d, $J = 5.2$ Hz, 2H), 7.37 (d, $J = 5.2$ Hz, 2H), 4.19 (d, $J = 5.6$ Hz, 4H), 1.78–1.86 (m, 1H), 1.66–1.74 (m, 1H), 1.56–1.64 (m, 2H), 1.46–1.56 (m, 2H), 1.25–1.45 (m, 12H), 1.03 (t, $J = 7.2$ Hz, 6H), 0.95 (t, $J = 7.2$ Hz, 6H).

2.4.7. *2,6-Bis(trimethyltin)-4,8-didodecyloxybenzo [1,2-b:4,5-b′] dithiophene (**M2**)*

A solution of *n*-butyllithium (7.7 ml, 19.25 mmol, 2.5 M in hexane) was added slowly to compound **4** (4.88 g, 8.75 mmol) in tetrahydrofuran (120 mL) at −78 °C. After addition, the mixture was stirred for 1 h at −78 °C. Trimethyltin chloride solution (20.4 mL, 20.4 mmol, 1.0 M in hexane) was added to the mixture. The mixture was warmed to room temperature and was stirred overnight. The reaction was quenched with addition of water (150 mL) and the mixture was extracted with diethyl ether for three times. The combined organic layer was dried with anhydrous sodium sulfate. Solvent was removed under reduced pressure and residue was purified by recrystallization in isopropanol to afford a white solid (6.37 g, 82.2%). ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.51 (s, 2H), 4.29 (t, $J = 6.5$ Hz, 4H), 1.86 (m, 4H), 1.57 (m, 4H), 1.23–1.37 (m, 32H), 0.88 (t, $J = 6.8$ Hz, 6H), 0.45 (s, 18H). ^{13}C (100 MHz, $CDCl_3$), δ (ppm): 143.32, 140.68, 134.27, 133.20, 128.27, 73.87, 32.20, 30.77, 29.96, 29.92, 29.76, 29.63, 26.36, 22.99, 14.43, −8.00.

2.4.8. *2,6-Bis(trimethyltin)-4,8-di(2-ethylhexyloxy)benzo [1,2-b:4,5-b′] dithiophene (**M3**)*

Same procedure was used as for compound **M2**. Compound used were *n*-butyllithium (10.56 ml, 26.4 mmol, 2.5 M in hexane), compound **5** (5.35 g, 12 mmol), trimethyltin chloride solution (27.96 mL 27.96 mmol, 1M in hexane). After workup, product was obtained as pale needle (7.07 g, 76.3%). ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.51 (s, 2H), 4.18 (d, 5.2 Hz, 4H), 1.78–1.86 (m, 1H), 1.66–1.74 (m, 1H), 1.56–1.64 (m, 2H), 1.46–1.56 (m, 2H), 1.28–1.45 (m, 12H), 1.02 (t, $J = 7.2$, 6H), 0.92 (t, $J = 7.2$, 6H), 0.45 (s, 18H). ^{13}C (100 MHz, $CDCl_3$), δ (ppm): 143.46, 140.81, 134.10, 133.10, 128.19, 75.84, 40.88, 30.75, 29.47, 24.12, 23.42, 14.45, 11.60, −8.11.

2.4.9. *Polymer **PBDTTPT1***

Tris(dibenzylideneacetone)dipalladium (0.015 g, 0.016 mmol) and triphenylarsine (0.0098 g, 0.032 mmol) were added to a solution of **M1** (0.78 g, 0.80 mmol) and **M2** (0.71, 0.80 mmol) in toluene (20 mL) under nitrogen. The solution was subjected to three cycles of evacuation and admission of nitrogen. The mixture was heated to 110 °C for 72 h. After cooled to room temperature, the mixture was poured into methanol (100 mL) and stirred for 2 h. A purple precipitate was collected by filtration. The product was purified by washing with methanol and hexane in a Soxhlet extractor for 24 h each. The residue was extracted with hot chloroform in an extractor for 24 h. After removing solvent, a purple solid was collected (0.98 g, 89.5%). M_n = 16.8 kDa; PDI = 1.59. ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.98 (br, 2H), 7.27 (br, 2H), 4.25 (br, 4H), 3.71(br, 2H), 2.5–2.7(br, 4H), 1.02–2.02 (br, 100H), 0.7–0.95 (br, 15H).

2.4.10. *Polymer **PBDTTPT2***

PBDTDPT2 are synthesized according to the same procedure as for **PBDTDPT1**. Compound used were Pd_2dba_3 (0.015 g, 0.016 mmol), triphenylarsine (0.098 g, 0.032 mmol), **M1** (0.78 g, 0.80 mmol) and **M3** (0.62 g, 0.80 mmol). After workup, a purple solid was obtained (0.87 g, 86.3%). M_n = 21.5 kDa; PDI = 1.84. ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.95 (br, 2H), 7.28 (br, 2H), 4.15 (br, 4H), 3.65 (br, 2H), 2.50–2.90 (br, 4H), 0.98–2.05 (br, 78), 0.70–0.95 (br, 21H).

3. Results and discussion

3.1. *Synthesis of polymers*

The synthetic routes for the monomers **M1**, **M2**, **M3** and polymers were illustrated in Scheme 1. The *N*-alkylated imide (**1**) was reacted with an excess amount of *N*-bromosuccinimide (NBS) to give the dibrominated imide (**2**) as a pale solid. The dibrominated imide (**2**) was reacted with 5-tri-*n*-butylstannyl-3-dodecylthiophene to give **3** by Stille coupling reaction. The compound **3** was halogenated by NBS in tetrahydrofuran to afford **M1** in 65.3% yield. The synthesis of benzo-dithiophenes were also outlined in Scheme 1. The tin containing monomers **M2** and **M3** were synthesized from compound **5** and **6** by lithiumation with *n*-butyllithium and quenching with trimethyltin chloride. The alternating polymer **PBDTTPT1** and **PBDTTPT2** were prepared by Stille coupling reaction with 1:1 monomer ratio in the presence of Pd_2dba_3 as catalyst and triphenylarsine as ligand to give **PBDTTPT1** (yield 89.5%) and **PBDTTPT2** (yield 86.3%). The crude copolymers were purified by precipitating in methanol and by washing with methanol and hexane in a Soxhlet. The number average molecular weights (M_n) of the copolymers were 16.8 kDa and 21.5 kDa with a polydispersity of 1.59 and 1.84 for **PBDTTPT1** and **PBDTTPT2**, respectively. Both copolymers showed good solubility in common organic solvents, such as tetrahydrofuran, dichloromethane and toluene.

3.2. *Thermal stability*

The thermal stabilities of copolymers were investigated by thermogravimetric analysis (TGA). The TGA plots of **PBDTTPT1**, and **PBDTTPT2** were showed in Fig. 1. The point of five percent weight loss was selected as the onset decomposition point. The thermal decomposition temperatures for **PBDTTPT1** and **PBDTTPT2** were determined around 352 °C under N_2 atmosphere. This indicates that the two copolymers have adequate thermal stability for application in polymer solar cells and other optoelectronic devices. Neither polymers displayed noticeable glass transition in differential scanning calorimetry (DSC) analysis.

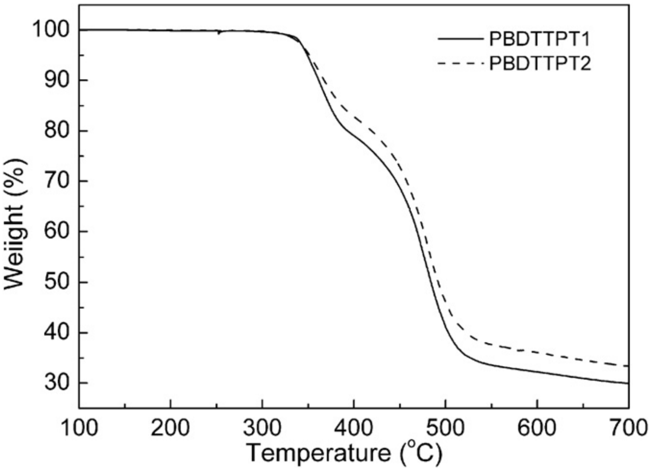

Fig. 1. TGA curves of the polymer **PBDTTPT1** and **PBDTTPT2**.

3.3. *Optical property*

The UV–vis absorption spectra of the copolymers in chloroform solution and as thin film were shown in Fig. 2. The optical absorption properties of the copolymers were listed in Table 1. The

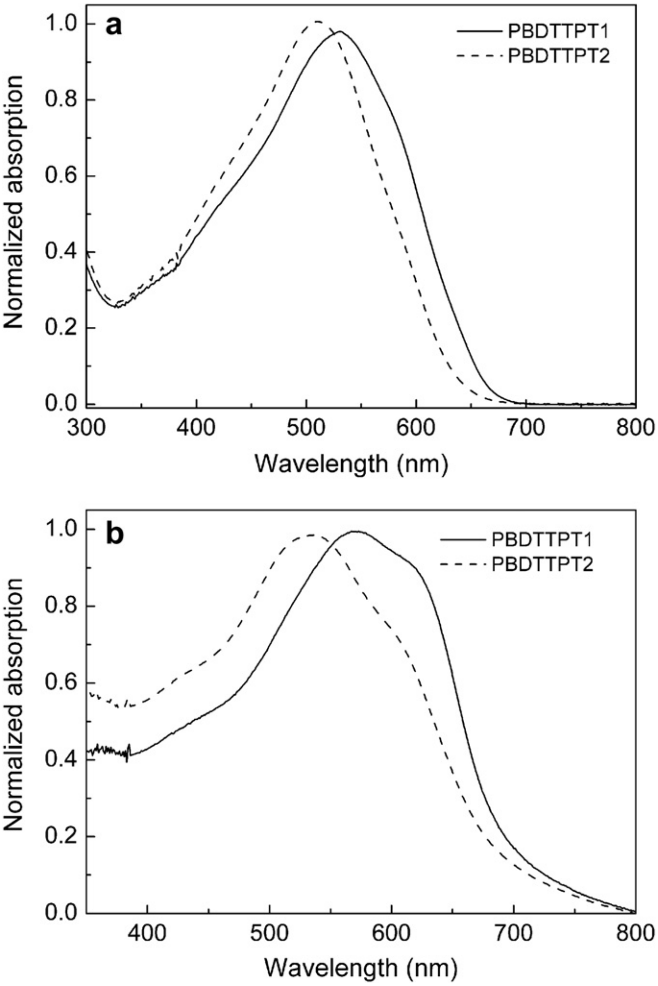

Fig. 2. Normalized UV–vis spectra of **PBDTTPT1** and **PBDTTPT2** (a) in chloroform solution and (b) as thin film.

Table 1
Optical and redox properties of **PBDTTPT1** and **PBDTTPT2**.

Polymer	Solution	Film			Film			
	$\lambda_{\max}^{abs}$ (nm)	$\lambda_{\max}^{abs}$ (nm)	λ_{onset}^{abs} (nm)	E_g^{opt} (eV)	E_{onset}^{ox} (V)	HOMO (eV)[a]	E_{onset}^{red} (V)[b]	LUMO (eV)[c]
PBDTTPT1	531	576	695	1.78	0.59	−5.30	−1.19	−3.52
PBDTTPT2	511	535	680	1.82	0.64	−5.35	−1.18	−3.53

[a] HOMO $= -(4.71 + E_{onset}^{ox})$.
[b] $E_{onset}^{red} = E_{onset}^{ox} - E_g^{opt}$.
[c] LUMO $= -(4.71 + E_{onset}^{red})$.

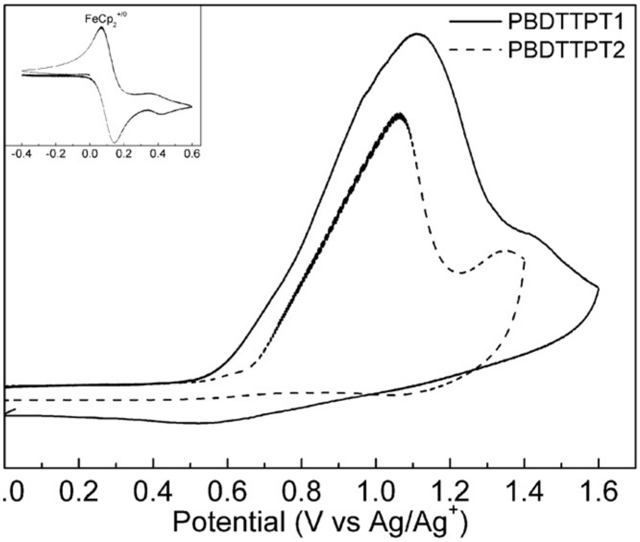

Fig. 3. Cyclic voltammograms of polymers thin film on a platinum electrode in Bu_4NPF_6/MeCN (0.1 M) at a scan rate of 100 mV/s.

maximal absorption of **PBDTTPT1** and **PBDTTPT2** were at 531 and 511 nm in solution, respectively. The two copolymers exhibited broad absorption between 350 and 700 nm, which resulted from intramolecular charge transfer (ICT) between the donor and acceptor units. The film absorption spectra of copolymers were depicted in Fig. 2b, the absorption maximums of **PBDTTPT1** and **PBDTTPT2** solid films were at 576 and 535 nm, respectively. The thin film absorption spectra of **PBDTTPT1** and **PBDTTPT2** were broadened. The absorption maximums were red-shifted about 35 and 24 nm in thin film comparing with those of the solution spectra. These indicated that the strong intermolecular interaction and aggregation occurred in solid-state of those polymers. The absorption spectra of **PBDTTPT1** (with all straight side chains) were red-shifted both in solution and as thin film compared with those of **PBDTTPT2** (with two ethylhexyl side chains). The branch alkyl chains of **PBDTTPT2** might prevent effective conjugation of the polymer. The optical bandgap (E_g^{opt}) was calculated from the absorption edge of solid-state film. The optical bandgap was 1.78 eV (absorption edge at 695 nm) for **PBDTTPT1** and 1.82 eV (absorption edge at 680 nm) for **PBDTTPT2**. Only a slight decrease in bandgap was observed compared with our previous reported polymer **PBDTDPT1** and **PBDTDPT2** (both of 1.84 eV) [25]. Unlike other reported system [26,27], incorporation of additional thiophene moieties into **BDT** and **DPT** system did not show significant change on the bandgaps of polymers. The steric hindrance of the alkyl side chains on thiophenes may introduce additional distortion on the main chain of polymers and disrupt conjugation.

3.4. *Electrochemical property*

The electrochemical properties of the copolymers were investigated by cyclic voltammetry (CV). The onset oxidations (HOMO energy level) were determined by CV. The CV curves of two copolymers film in acetonitrile containing tetra-*n*-butylammonium hexafluorophosphate (0.1 M) at a potential scan rate of 100 mV/s were shown in Fig. 3. The potentials were referenced to the ferrocene/ferrocenium redox couple (Fc/Fc$^+$). It was assumed that the redox potential of Fc/Fc$^+$ had an absolute energy level of −4.8 eV to vacuum [32]. The potential of Fc/Fc$^+$ was measured under the same conditions and located at 0.09 V related to the Ag/Ag$^+$ electrode. The CV data were summarized in Table 1. The onset oxidation potential of **PBDTTPT1** and **PBDTTPT2** were located at 0.59 and 0.64 eV, respectively. The HOMO energy levels of copolymer **PBDTTPT1** and **PBDTTPT2** were calculated to be −5.30 and −5.35 eV. The HOMO energy levels of **PBDTTPT1** and **PBDTTPT2** are slightly higher than polymer **PBDTDPT**s (−5.42 and 5.44 eV) [25]. The small increasing of HOMO energy levels was resulted from the addition of electron rich alkyl-substituted thiophene units. The similar results were reported before [27,33]. The relatively low HOMO energy level of two copolymers are desirable for achieving higher open-circuit voltage when they are used as donors blended with PCBM in PSCs. The relative lower HOMO energy levels in these new polymers can be attributed to electron deficient imide group

Table 2
Devices performance of polymers solar cells.

Weight ratio	**PBDTTPT1**: $PC_{71}BM$				**PBDTTPT2**: $PC_{71}BM$			
	1:1	1:2	1:3	2:1	1:1	1:2	1:3	2:1
J_{sc} (mA/cm^2)	3.04	2.06	1.73	2.18	3.93	3.12	2.20	2.49
V_{oc} (V)	0.89	0.88	0.88	0.92	0.92	0.93	0.93	0.95
FF	0.62	0.60	0.58	0.53	0.57	0.56	0.56	0.50
PCE (%)	1.68	1.09	0.89	1.08	2.05	1.62	1.14	1.18

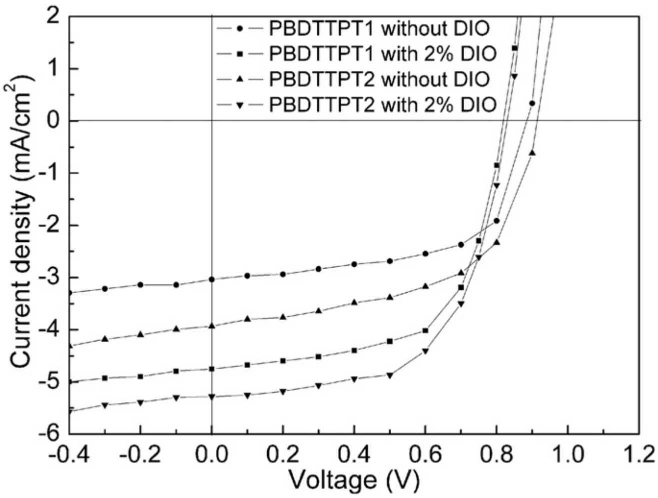

Fig. 4. Current-voltage characteristics of polymers/$PC_{71}BM$ solar cells under illumination of AM 1.5G, 100 mW/cm^2.

Table 3
Devices performance of polymers solar cells with and without processing additive.

	PBDTTPT1: $PC_{71}BM = 1:1$		**PBDTTPT2**: $PC_{71}BM = 1:1$	
	No DIO	2% DIO	No DIO	2% DIO
J_{sc} (mA/cm^2)	3.04	4.75	3.93	5.28
V_{oc} (V)	0.89	0.82	0.92	0.83
FF	0.62	0.62	0.57	0.61
PCE (%)	1.68	2.43	2.05	2.68

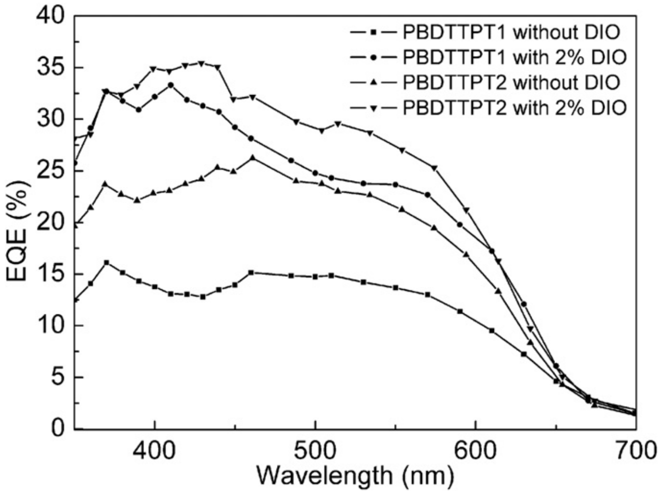

Fig. 5. External quantum efficiency of polymer/$PC_{71}BM$ blends.

on **TPT** unit. The LUMO energy levels of **PBDTTPT1** and **PBDTTPT2** were −3.52 and −3.53 eV which were calculated from the optical bandgap and HOMO energy levels of the polymers.

3.5. Photovoltaic property

The photovoltaic properties of polymer **PBDTTPT1** and **PBDTTPT2** were evaluated in BHJ solar cell devices. The copolymers were used as donors and $PC_{71}BM$ was used as electron acceptor. The device structures were ITO/PEDOT: PSS/Polymer:PCBM/LiF/Al. Solar cells were characterized under AM 1.5G illumination at 100 mW/cm^2 from a solar simulator. The photovoltaic performance of the devices based on the blend of copolymers and $PC_{71}BM$ at deference weight ratio were summarized in Table 2. The short-circuit current densities (J_{sc}) of devices were varied at different weight ratio of donor polymer to $PC_{71}BM$. The weight ratios were optimized for device performance. The changing the weight ratio of donor polymer to $PC_{71}BM$ had little influence on open circuit voltage (V_{oc}). The highest V_{oc} of 0.95 V was achieved with blend of **PBDTTPT2**: $PC_{71}BM$ (wt. ratio of 2: 1). The optimized devices had J_{sc} of 3.04 and 3.93 mA/cm^2, V_{oc} of 0.89 and 0.92 V, which yield PCE of 1.68% and 2.05% for **PBDTTPT1** and **PBDTTPT2**, respectively. Adding a small amount of diiodooctane (DIO) to the blend of copolymer and PCBM before spin-coating significantly improved the efficiency of the cells. The current density-voltage (J-V) curves of the devices based on the polymers: $PC_{71}BM$ blend with additive (DIO, 2% by volume) were presented in Fig. 4 and the data were summarized in Table 3. The enhanced J_{sc} and PCE value were observed in both **PBDTDPT1** and **PBDTDPT2** based devices, the devices with DIO had the J_{sc} of 4.75 and 5.28 mA/cm^2, the PCE of 2.43% and 2.68% for **PBDTTPT1** and **PBDTTPT2**, respectively. This increasing of performance was attributed to the improvement of charge separation in BHJ [34]. The external quantum efficiency (EQE) of the optimized devices with and without DIO were shown in Fig. 5. The EQE of devices processed with DIO and without DIO were very different in the region of 350–700 nm. The EQE values of devices with DIO processing additives are much higher in this region and result the higher J_{sc}.

4. Conclusions

We have successfully synthesized two new low bandgap copolymers by incorporation of additional alkylthiophene moieties into the **BDT** and **DPT** system. The new polymers show good solubility in common organic solvent, high thermal stability and broad absorption in the region from 350 to 700 nm. The effect of incorporation of additional alkylthiophene units on the optical, electrochemical and photovoltaic properties of polymers were studied. Only a slight decreasing in bandgap was observed in new polymers compared with our previous reported copolymer **PBDTDPTs**. The devices based on the blends of new copolymers and $PC_{71}BM$ exhibited V_{oc} of 0.82–0.95 V. The PCEs of devices with the copolymer: $PC_{71}BM$ (wt. ratio of 1: 1) achieved 2.43% for **PBDTTPT1** and 2.68% for **PBDTTPT2** under the illumination of AM 1.5G, 100 mW/cm^2. The results indicate that these new copolymers with high V_{oc} might become useful materials for organic solar cells applications.

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References

[1] Peet J, Kim JY, Coates NE, Ma WL, Moses D, Heeger AJ, et al. Nat Mater 2007;6: 497–500.
[2] Kim JY, Lee K, Coates NE, Moses D, Nguyen TQ, Dante M, et al. Science 2007;317:222–5.
[3] Invernale MA, Bokria JG, Ombaba M, Lee K-R, Mamangun DMD. Polymer 2010;51:378–82.
[4] Brabec CJ, Sariciftci NS, Hummelen JC. Adv Funct Mater 2001;11:15–26.
[5] Yildirim M, Kaya I. Polymer 2009;50:5653–60.
[6] Hou J, Chen H-Y, Zhang S, Li G, Yang Y. J Am Chem Soc 2008;130:16144–5.
[7] Liu Y, Chen X, Qin J, Yu G, Liu Y. Polymer 2010;51:3730–5.
[8] Kumar AK, Jang S-Y, Padilla J, Otero TF, Sotzing GA. Polymer 2008;49: 3686–92.
[9] Yu G, Gao J, Hummelen JC, Wudl FA, Heeger AJ. Science 1995;270:1789–91.
[10] Coakley K, Mcgehee MD. Chem Mater 2004;16:4533–42.
[11] Xin H, Guo XG, Kim FS, Ren G, Waston MK, Jenekhe SA. J Mater Chem 2009;19:5303–10.
[12] Blouin N, Michaud A, Leclerc M. Adv Mater 2007;19:2295–300.
[13] Chen JW, Cao Y. Acc Chem Res 2009;42:1709–18.
[14] Qin RP, Li WW, Li CH, Du C, Veit C, Schleiermacher H-F, et al. J Am Chem Soc 2009;131:14612–3.
[15] Scharber MC, Muhlbacher D, Koppe M, Denk P, Waldauf C, Heeger AJ, et al. Adv Mater 2006;18:789–94.
[16] Bredas J-L, Beljonne D, Coropceanu V, Cornil J. Chem Rev 2004;104: 4971–5004.
[17] Park SH, Roy AJ, Beaupre S, Cho S, Coates N, Moon JS, et al. Nat Photon 2009;3:297–303.
[18] Wang E, Wang L, Lan L, Luo C, Zhuang W, Peng J, et al. Appl Phys Lett 2008;92: 033307.
[19] Huang F, Chen K-S, Yip H-L, Hau SK, Acton O, Zhang Y, et al. J Am Chem Soc 2009;131:13886–7.
[20] He Y, Chen H-Y, Hou J, Li YF. J Am Chem Soc 2010;132:1377–82.
[21] Yuan M-C, Chiu M-Y, Liu S-P, Chen C-M, Wei K-H. Macromolecules 2010;43:6936–8.
[22] Zou Y, Najari A, Berrouard P, Beaupre S, Aich BR, Tao Y, et al. J Am Chem Soc 2010;132:5330–1.
[23] Piliego C, Holcombe TW, Douglas JD, Woo CH, Beaujuge PM, Frecher JMJ. J Am Chem Soc 2010;132:7595–7.
[24] Zhang Y, Hau SK, Yip H-L, Sun Y, Acton O, Jen AK-Y. Chem Mater 2010;22: 2696–8.
[25] Zhang G, Fu Y, Xie Z, Zhang Q. Chem Commun 2010;46:4997–9.
[26] Bundgaard E, Krebs FC. Macromolecules 2006;39:2823–31.
[27] Yue W, Zhao Y, Tian H, Song D, Xie Z, Yan D, et al. Macromolecules 2009;42: 6510–8.

[28] Biniek L, Chochos CL, Hadziioannou G, Leclerc N, Leveque P, Heiser T. Macromol Rapid Commun 2010;31:651–6.
[29] Hou J, Park MH, Zhang S, Yao Y, Chen LM, Li JH, et al. Macromolecules 2008;41:6102–8.
[30] Nielsen CB, Bjornholm T. Org Lett 2004;6:3381–4.
[31] Zoombelt AP, Gilot J, Wienk MM, Janssen RAJ. Chem Mater 2009;21:1663–9.
[32] Li YF, Cao Y, Gao J, Wang D, Yu G, Heeger AJ. Syn Met 1999;99:243–8.
[33] Price SC, Stuart AC, You W. Macromolecules 2010;43:4609–12.
[34] Lee JK, Ma LW, Brabec CJ, Yuen J, Moon JS, Kim JY, et al. J Am Chem Soc 2008;130:3619–23.