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# Synthesis of conjugated polymers with broad absorption bands and photovoltaic properties as bulk heterojuction solar cells

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ABSTRACT

Two new broad absorbing alternating copolymers, poly[1-(2,6-diisopropylphenyl)-2,5-bis(2-thienyl)pyrrole-*alt*-4,7-bis(3-octyl-2-thienyl)benzothiadiazole] (**PTPTTBT-P1**) and poly[1-(*p*-octylphenyl)-2,5-bis(2-thienyl)pyrrole-*alt*-4,7-bis(3-octyl-2-thienyl)benzothiadiazole] (**PTPTTBT-P2**), were prepared via Suzuki polycondensation with high yields. The two polymers were found to show characteristic absorption in the visible region of the solar spectrum. Interestingly the absorption of **PTPTTBT-P1** was found to cover the visible region from 350 to 650 nm with the broad and flat absorption maximum from 440 to 510 nm in film and the absorption of **PTPTTBT-P2** was found to cover the visible region from 350 to 950 nm with the relatively distinct absorption maxima at 425 and 522 nm and very weak absorption maximum at 832 nm in film. The electrochemical band gaps of the polymers were calculated to be 1.88 eV and 1.87 eV, respectively, while the optical band gaps of the polymers were calculated to be 1.94 eV and 1.87 eV, respectively. The photovoltaic properties of polymers were investigated with bulk heterojunction (BHJ) solar cells fabricated in ITO/PEDOT:PSS/polymer:$PC_{70}BM$(1:5 wt%)/TiOx/Al configurations. The maximum power conversion efficiency (PCE) of the solar cell composed of **PTPTTBT-P1**:$PC_{70}BM$ as an active layer was 1.57% with current density ($J_{sc}$) of 8.17 mA/cm$^2$, open circuit voltage ($V_{oc}$) of 0.52 V and fill factor (FF) of 36%.

## 1. Introduction

Conjugated polymer-based bulk heterojunction (BHJ) solar cells have been extensively studied because they have several advantageous properties such as fast charge dissociation and charge separation, solution processability, flexibility and cost-effective large-area manufacturing [1–7]. In the beginning of BHJ solar cell development, the blends of poly (3-hexylthiophene) (P3HT) and [6,6]-phenyl $C_{61}$ butyric acid methyl ester ($PC_{61}BM$) were efficiently employed as photoactive layers and the power conversion efficiencies (PCEs) were achieved up to 5% [8–10]. The insufficient solar flux harvesting by P3HT might be the crucial factor limiting the PCEs. To overcome the insufficient solar flux harvesting by P3HT, various low band gap copolymers were prepared [11–26] and the PCE was improved up to 7.4% [23]. To improve the PCEs further, development of new semiconducting polymers having broader absorption with high molar absorption coefficient is important.

We have been interested in the preparation of pyrrole-containing π-conjugated polymers for BHJ solar cell applications. While pyrrole-containing π-conjugated polymers have been rarely studied for BHJ solar cell applications, a pyrrole-containing oligomer (PTPTB) incorporating 2,5-bis(2-thienyl)-*N*-dodecylpyrrole (*N*-dodecyl TPT) and 2,1,3-bezothiadiazole was applied to solar cell fabrications [27,28]. The BHJ solar cells fabricated from the blends of PTPTB oligomer and PCBM as an active layer were found to show the PCEs of up to 1.0% [28]. In order to enhance electron donating strength and light harvesting properties of *N*-dodecyl TPT, we incorporated aryl groups such as 2,6-diisopropylphenyl or 4-octylpheneyl group on the pyrrole nitrogen instead of dodecyl group. Indeed, the molar absorptivities of *N*-aryl TPTs such as 1-(2,6-diisopropylphenyl)-2,5-di(5-bromo-2-thienyl)pyrrole and 1-(4-octylphenyl)-2,5-di(5-bromo-2-thienyl)pyrrole were greater than that of *N*-dodecyl TPT [29]. In addition, the absorption maxima of *N*-aryl TPTs were red-shifted compared to that of *N*-dodecyl TPT [29]. *N*-Aryl TPTs have been copolymerized with tetraoctylindenofluorene, 2,5-dioctyloxy phenylene or 3-octylthiophene and the resulting π-conjugated TPT-based copolymers have been applied to

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the fabrication of BHJ solar cells [29,30]. The BHJ solar cells fabricated from the blend of the *N*-aryl TPT-based copolymer and [6,6]-phenyl-$C_{70}$-butyric acid methyl ester ($PC_{70}BM$) as a photoactive layer showed the PCE of 1.35% with high current density ($J_{sc} = 7.4$ mA/cm$^2$) [30].

As an effort to utilize *N*-aryl TPT units further in BHJ solar cells, we were interested in synthesizing *N*-aryl TPT-based broad absorption polymers. Usually the polymers developed by copolymerizing D–A–D (donor–acceptor–donor) segment, especially thiophene-benzothiadiazole-thiophene (TBT) segment, with electron rich unit such as carbazole, fluorene, [3,2-b]thienothiophene, alkyl thiophene or phenothiazine have been known to show broad absorption in the region of 300 –700 nm, due to the combined electronic transitions such as $\pi-\pi^*$ electronic transition and internal charge transfer (ICT) between the donor and acceptor moiety [31–38]. Consequently, we can expect that the copolymers prepared by copolymerizing *N*-aryl TPT unit with TBT unit would show broad absorption. Based on this expectation, in this study, we copolymerized the *N*-aryl TPT monomers with an alkylated TBT monomer and obtained two copolymers such as **PTPTTBT-P1** and **PTPTTBT-P2** (Scheme 1). The two polymers were found to show characteristic absorption in the visible region of the solar spectrum. In this paper, we wish to report the synthesis of the two new alternating copolymers, **PTPTTBT-P1** and **PTPTTBT-P2**, and their BHJ solar cell applications.

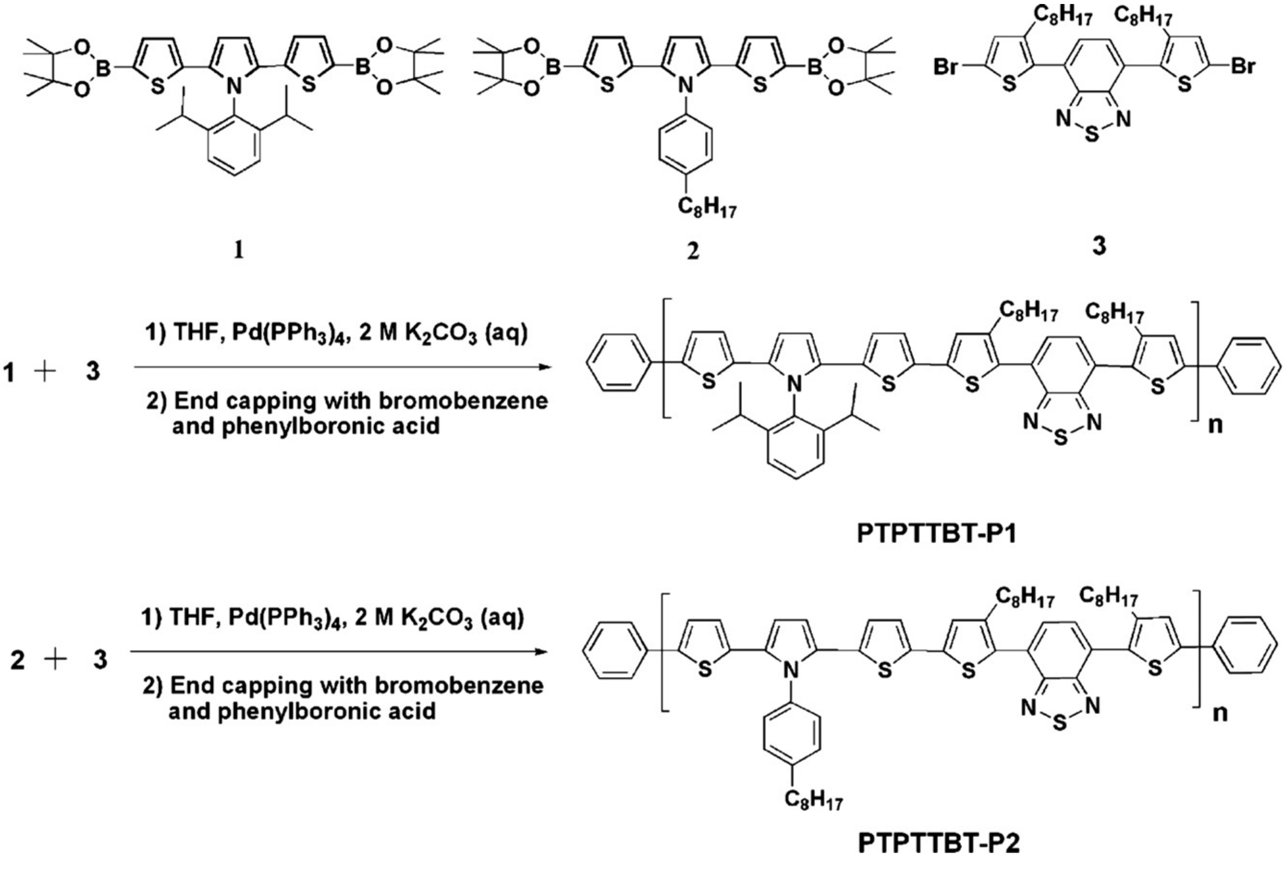
## 2. Experimental section

### 2.1. Materials and instruments

All reagents were purchased from Aldrich or TCI chemicals and used without further purification. Solvents were purified by normal procedure and handled in a moisture-free atmosphere. Flash column chromatography was performed using silica gel (Merck Kieselgel 60, 70–230 mesh). The $^1$H and $^{13}$C NMR spectra were measured using a Varian Mercury Plus 300 spectrometer with chloroform as an internal standard. The optical studies such as absorption and photoluminescence were performed by using JASCO V-570 spectrophotometer and Hitachi F-4500 fluorescence spectrophotometer. The thermogravimetric analysis (TGA) of the polymers was performed with a Mettler Toledo Labsys TG/DSC-1600 analyzer under a nitrogen atmosphere at a heating rate of 10 °C/min. Agilent 1100 series liquid chromatography system connected with PLgel 5 μm MIXED-C column was employed in the molecular weight and polydispersity index (PDI) determination, and the gel permeation chromatography (GPC) system performance was verified by polystyrene standard calibration. The electrochemical studies of the polymers were performed on a CH Instruments Electrochemical Analyzer. Atomic force microscopy (AFM) images of blend films were obtained on a Veeco-Multimode AFM operating in the tapping mode.

### 2.2. Device fabrication and characterization of BHJ solar cells

The BHJ solar cell devices were fabricated by the known procedure reported previously in our laboratory [29,30] and the method is shortly summarized as following. The active layer (80 nm thickness) composed of electron donor (polymer) and acceptor ($PC_{70}BM$) in a ratio of 1:5 wt% was sandwitched between the hole injecting and hole blocking layers such as poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) and TiOx. The substrate was covered with ITO anode and aluminum cathode and the short circuit was made between the electrodes. The



**Scheme 1.** Synthetic route for the synthesis of polymers **PTPTTBT-P1** and **PTPTTBT-P2**.

photovoltaic device was then subjected to annealing at 100 °C for 30 min. The top metal electrode area comprising the active area of the solar cells was 4 mm$^2$. The device performance was measured using an AM 1.5G solar simulator (Oriel 300 W) at 100 mW/cm$^2$ light illumination. The light intensity was adjusted using Oriel power meter (model No. 70260 which was calibrated using laboratory standards that are traceable to the National Institute of Standards and Technologies, USA) before the measurements were carried out. The *J*–*V* curves were recorded using a standard source measurement unit (Keithley 236). Thickness of the thin films was measured using a KLA Tencor Alpha-step IQ surface profilometer with an accuracy of ±1 nm.

### *2.3. Synthesis of polymers*

Polymers **PTPTTBT-P1** and **PTPTTBT-P2** were prepared as shown in Scheme 1. The detailed synthetic procedures are as follows.

#### *2.3.1. 1-(p-Octylphenyl)-2,5-bis(5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-thienyl)pyrrole (**2**)*

Monomer **2** was prepared in 77% yield by the same procedure as reported for the synthesis of monomer **1** [30] by treating 1-(*p*-octylphenyl)-2,5-di(2-thienyl-5-bromo)pyrrole, which was prepared by the known procedure [29], with *n*-BuLi and then with 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane. mp 169–170 °C; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ (ppm) 7.29 (d, 2H), 7.21 (d, 4H), 6.59 (s, 2H), 6.37 (d, 2H), 2.69 (t, 2H), 1.58–1.68 (m, 2H), 1.18–1.38 (m, 34H), 0.89 (t, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ (ppm) 144.4, 142.2, 137.7, 136.1, 130.8, 129.7, 129.6, 125.3, 111.0, 84.2, 35.9, 32.1, 31.6, 29.6, 29.5, 22.3, 25.1, 25.0, 22.9, 14.4; HRMS (EI, *m*/*z*) [M] Calcd for $C_{38}H_{51}B_2NO_4S_2$ 671.3446, found 671.3451; Anal. Calcd for $C_{38}H_{51}B_2NO_4S_2$: C, 67.96; H, 7.65; N, 2.09; S, 9.55. Found: C, 67.11; H, 7.72; N, 2.19; S, 9.74.

#### *2.3.2. 4,7-Bis(5-bromo-3-Octyl-2-thienyl)-2,1,3-benzothiadiazole (**3**)*

4,7-Bis(3-octyl-2-thienyl)-2,1,3-benzothiadiazole (2.62 g, 5.0 mmol), which was synthesized according to the known literature procedure [39], was dissolved in dimethylformamide (60 mL) under argon in the dark. To the solution was added *N*-bromosuccinimide (NBS) (1.78 g, 10.0 mmol) portion wise. The resulting solution was stirred at room temperature under $N_2$ overnight. The solvent was concentrated by using rotary evaporator and then the crude martial was dissolved in diethyl ether and the organic solution was washed with water and then brine. The organic solution was dried with sodium sulfate, filtered and the solvent was evaporated under reduced pressure and further dried under high vacuum. The compound was purified by flash column chromatography using 10% ethyl acetate in hexane. Monomer **3** was obtained as a yellow paste (3.0 g, 88%). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 7.60 (s, 2H), 7.06 (s, 2H), 2.60 (t, 4H), 1.52–1.66 (m, 4H), 1.08–1.32 (m, 20H), 0.85 (t, 6H). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 154.1, 142.6, 133.7, 132.1, 129.8, 126.8, 113.3, 32.1, 30.6, 29.8, 29.6, 29.6, 29.5, 22.8, 14.2; HRMS (EI, *m*/*z*) [M] Calcd for $C_{30}H_{38}Br_2N_2S_3$ 680.0564, found 680.0569; Anal. Calcd for $C_{30}H_{38}Br_2N_2S_3$: C, 52.78; H, 5.61; N, 4.10; S, 14.09. Found: C, 52.21; H, 6.12; N, 4.56; S, 13.88.

#### *2.3.3. Polymerization*

Monomers **1** (0.19 g, 0.30 mmol) and **3** (0.20 g, 0.30 mmol) were taken for the preparation of polymer **PTPTTBT-P1** and monomers **2** (0.20 g, 0.3 mmol) and **3** (0.20 g, 0.3 mmol) were employed for the preparation of polymer **PTPTTBT-P2**. A respective monomer mixture in toluene (60 mL) was purged well with $N_2$ for 45 min. $Pd(PPh_3)_4$ (0.02 g, 5 mol%) and aqueous 2 M $K_2CO_3$ (7 mL) were added to the solution and then the whole solution was refluxed for 48 h with vigorous stirring under argon. To the refluxing solution was added phenyl boronic acid (50 mg) and the whole mixture was refluxed for 6 h and then was added bromobenzene (0.1 mL) and the resulting reaction mixture was refluxed again for 12 h. The solvent was concentrated and cooled to room temperature. The cooled mixture was then poured drop by drop into methanol:water mixture (200 mL:100 mL) with vigorous stirring. The precipitate was recovered by filtration and washed well with 2 N HCl, and then the solid was extracted with methanol for 24 h and, then with acetone for 24 h in a Soxhlet apparatus to afford **PTPTTBT-P1** or **PTPTTBT-P2** as a solid material. **PTPTTBT-P1**: dark brown color solid. Yield (0.22 g, 83%). $^1$H NMR (300 MHz, CDCl3): $\delta$ 7.54–7.68 (m, 3H), 7.28 (d, 2H), 7.03 (s, 2H), 6.87 (d, 2H), 6.66 (s, 2H), 6.13 (d, 2H), 2.42–2.68 (m, 6H), 1.43–1.72 (m, 4H), 1.22 (d, 20H), 0.78–0.98 (m, 18H); Anal. Calcd for $C_{54}H_{61}N_3S_5$: C, 71.09; H, 6.74; N, 4.61; S, 17.57. Found: C, 70.04; H, 6.65; N, 4.05; S, 17.94. **PTPTTBT-P2**: brown color solid. Yield (0.22 g, 79%). $^1$H NMR (300 MHz, CDCl3): $\delta$ 7.61 (s, 2H), 7.28 (d, 4H), 7.04 (s, 2H), 6.92 (d, 2H), 6.60 (d, 2H), 6.36 (d, 2H), 2.51–2.62 (m, 6H), 1.51–55 (m, 6H), 1.22 (d, 30H), 0.85 (t, 9H); Anal. Calcd for $C_{56}H_{65}N_3S_5$: C, 71.52; H, 6.97; N, 4.47; S, 17.05. Found: C, 71.04; H, 6.68; N, 4.98; S, 17.68.

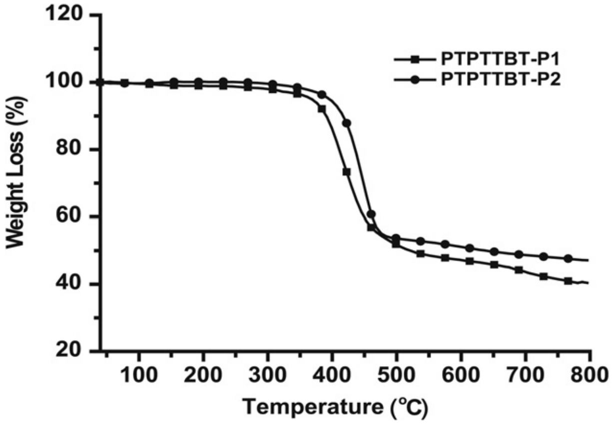


**Fig. 1.** TGA curves of copolymers **PTPTTBT-P1** and **PTPTTBT-P2**.

**Table 1**
Polymerization results and thermal, optical and electrical properties of **PTPTTBT-P1** and **PTPTTBT-P2**.

| | | PTPTTBT-P1 | PTPTTBT-P2 |
|---|---|---|---|
| $M_w \times 10^4$ [a] | | 1.54 | 2.13 |
| PDI[a] | | 1.61 | 1.75 |
| TGA ($T_d$)[b] | | 369 | 392 |
| Abs $\lambda_{max}$ (nm) | Solution[c] | Broad and flat (440–490) | 415, 487, 805 |
| | Film[d] | Broad and flat (440–510) | 425, 522, 832 |
| HOMO[e] (eV) | | −5.39 | −5.31 |
| LUMO [e] (eV) | | −3.51 | −3.44 |
| $E_g$[f] (eV) | | 1.88 | 1.87 |
| $E_g$[g] (eV) | | 1.94 | 1.87 (or 1.28) |

[a] Weight average molecular weight ($M_w$) and polydispersity (PDI) of the polymers were determined by GPC using polystyrene standards.
[b] Onset decomposition temperature (5% weight loss) measured by TGA under $N_2$.
[c] Measured in chloroform solution.
[d] Measured in thin film on quartz.
[e] HOMO and LUMO energy levels were estimated from the cyclic voltammetry analysis.
[f] Electrochemical band gaps calculated from the HOMO–LUMO energy levels.
[g] Optical energy band gaps estimated from the onset wavelength of the optical absorption in thin film.

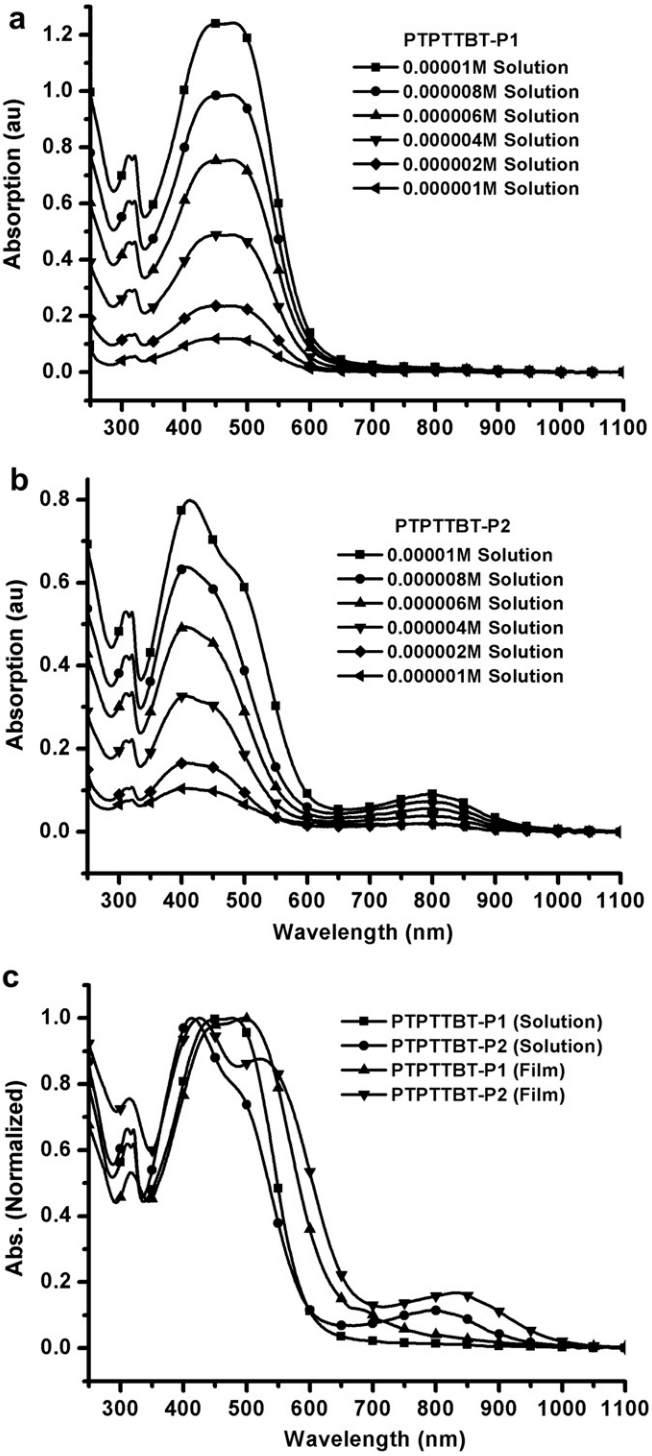


**Fig. 2.** Concentration dependent UV–visible absorption spectra of polymers **PTPTTBT-P1** (a) and **PTPTTBT-P2** (b) in chloroform and normalized absorption spectra of polymers **PTPTTBT-P1** and **PTPTTBT-P2** in chloroform and in thin film on quartz (c).

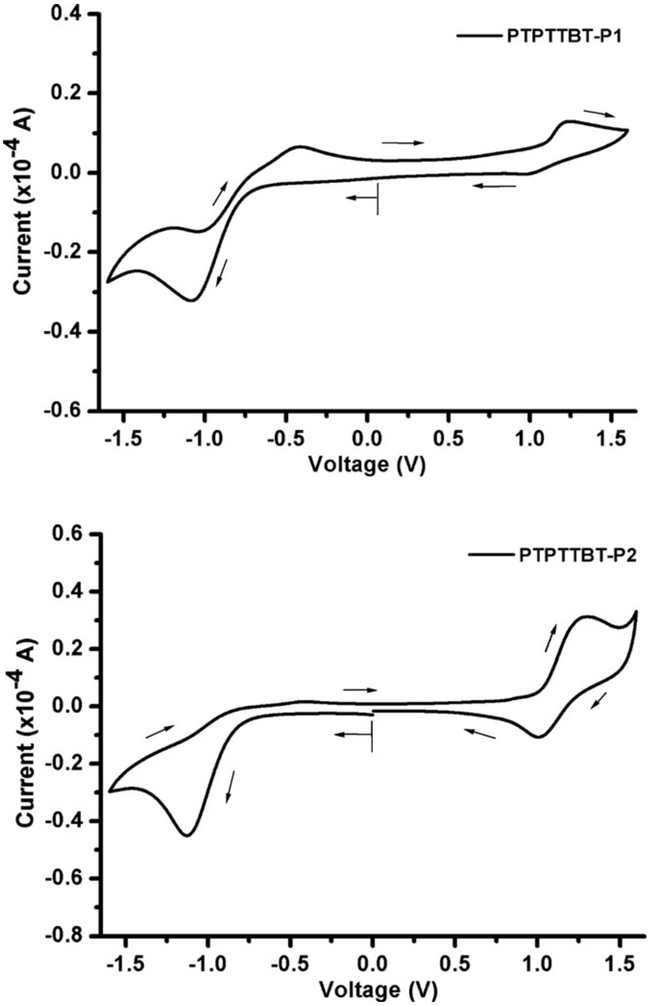


**Fig. 3.** Cyclic voltammograms of polymers **PTPTTBT-P1** (top) and **PTPTTBT-P2** (bottom) films cast on platinum working electrode in 0.1 M TBATFB/acetonitrile at a scan rate of 100 mV/s.

## 3. Results and discussions

### 3.1. Synthesis and characterization of polymers

Electron rich *N*-aryl TPT monomer **1** was prepared via the procedure reported previously [30]. Electron rich *N*-aryl TPT monomer **2** was prepared by simply treating 1-(*p*-octylphenyl)-2,5-di(2-thienyl-5-bromo)pyrrole with *n*-BuLi and then with 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane. Electron deficient TBT monomer **3** was synthesized by treating 4,7-bis-(3-octyl-2-thienyl)-2,1,3-bezothiadiazole, which was prepared via the reported procedure [39], with NBS. The usual Suzuki coupling between monomers **1** and **3** or monomers **2** and **3** and then end-capping with phenyl boronic acid and then with bromobenzene were employed for the preparation of alternating copolymers **PTPTTBT-P1** and **PTPTTBT-P2**. The two copolymers thus prepared were purified by Soxhlet extraction and characterized by using NMR, elemental analysis and GPC. The solubility of the copolymers was found to be quite good in common organic solvents such as chloroform, chlorobenzene, dichlorobenzene, tetrahydrofuran and toluene. The weight average molecular weight ($M_w$) and PDI of copolymer **PTPTTBT-P1** were $1.54 \times 10^4$ and 1.61, respectively, and those of copolymer **PTPTTBT-P2** were $2.13 \times 10^4$ and 1.75, respectively. From the thermogravimetric analysis (TGA), the 5% weight loss temperatures of the two copolymers were found to be 369 °C and 392 °C, respectively, indicating the two polymers are thermally quite stable. Fig. 1 represents the TGA curves of the copolymers. The polymerization results and thermal properties of polymers **PTPTTBT-P1** and **PTPTTBT-P2** are summarized in Table 1.

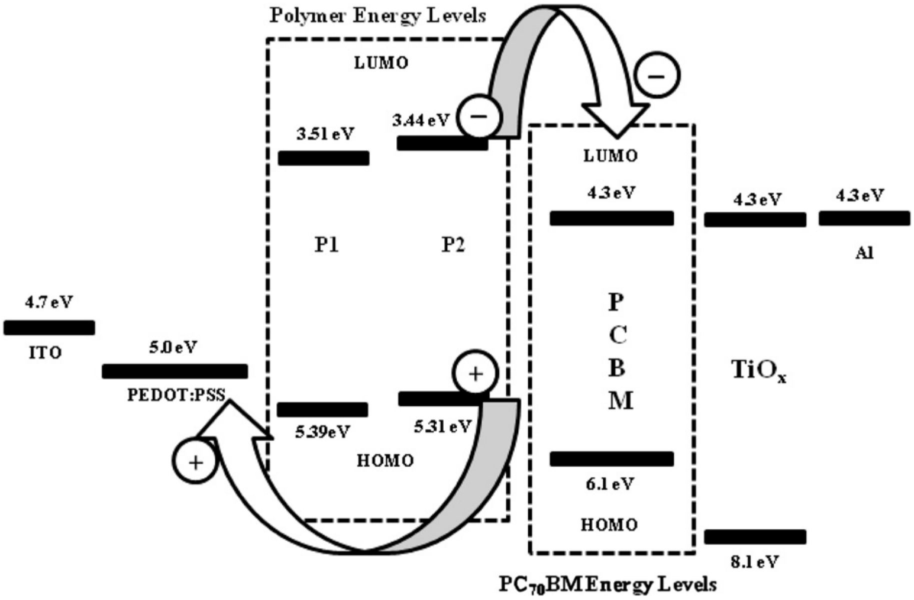


**Fig. 4.** The energy level diagram of polymers **PTPTTBT-P1**, **PTPTTBT-P2** and **PC$_{70}$BM** with all other materials used in BHJ solar cell.

### 3.2. Optical properties

The concentration dependent UV–visible absorption spectra of the polymers in chloroform solution and the normalized UV–visible absorption spectra of the polymers measured in chloroform and as thin films (on quartz) at room temperature are shown in Fig. 2 (a)–(c). The concentration dependent UV–visible spectra of the polymers shown in Fig. 2(a) and (b) clearly show that the absorption increase continuously as the concentration of the polymer solution in chloroform is increased. However, the absorption intensity of polymer **PTPTTBT-P1** is about 1.5 times greater than that of polymer **PTPTTBT-P2**. In addition, the absorption spectrum of polymer **PTPTTBT-P1** is quite interesting in that it shows the quite broad absorption from 350 nm to 650 nm with broad and flat absorption maximum from 440 nm to 490 nm in chloroform and the quite broad absorption from 350 nm to 700 nm with broad and flat absorption maximum from 440 to 510 nm in thin film. The broad and flat absorption maximum of copolymer **PTPTTBT-P1** might be resulted from the overlap of the two $\pi$–$\pi^*$ electronic transitions of the very similar absorption strength originated from the *N*-aryl TPT segment and the TBT segment. The broad and flat absorption maximum of polymer **PTPTTBT-P1** in film is expected to induce the effective solar flux harvesting in the region from 440 nm to 510 nm. In contrast, polymer **PTPTTBT-P2** shows the three distinct absorption maxima, two of them in high energy part and one in low energy part of the solar spectrum. The absorption maxima of polymer **PTPTTBT-P2** in film state were found to be at 425 nm, 522 nm and 832 nm whereas those in solution state were found to be at 415 nm, 487 nm and 805 nm, respectively. The short wavelength absorption maximum is expected to be attributed to the $\pi$–$\pi^*$ electronic transition of the *N*-aryl TPT segment and the middle wavelength absorption maximum is expected to be attributed to the $\pi$–$\pi^*$ electronic transition of the TBT segment. In polymer **PTPTTBT-P2**, the overlap of the two $\pi$–$\pi^*$ electronic transitions originated from the *N*-aryl TPT segment and the TBT segment is not so effective because the absorption strengths of the two $\pi$–$\pi^*$ electronic transitions originated from the *N*-aryl TPT segment and the TBT segment are quite different. Consequently, two absorptions at the short and middle wavelength are observed. The very weak absorption at 805 nm in solution state or at 832 nm in film state might be originated from the donor–acceptor internal charge transfer (ICT) between the thiophene-based units, as the electron donor, and the benzothiadiazole moiety, as the electron acceptor [31,33,38]. According to simple calculation with Gaussian 03W computer molecular modeling software, the dihedral angle between the thiophene group and the *N*-arylpyrrole group of the *N*-(2,6-diisopropylphenyl) TPT unit was found to be greater than that of the *N*-(*p*-octylphenyl) TPT unit and consequently, the coplanarity of polymer **PTPTTBT-P1** is expected to be less than that of polymer **PTPTTBT-P2**. In this instance, polymer **PTPTTBT-P1** seems not to have the peak around 800 nm originated from ICT. The optical band gap calculated from the onset absorption wavelength (638 nm) of **PTPTTBT-P1** in film state was 1.94 eV. The optical band gap calculated from the onset wavelength (968 nm) of the very weak absorption at 832 nm of **PTPTTBT-P2** in film state was 1.28 eV. However, the optical band gap calculated from the onset wavelength (664 nm) of the absorption at 522 nm of **PTPTTBT-P2** in film state was 1.87 eV. The optical properties of the polymers were summarized in Table 1.

### 3.3. Electrochemical properties

The electrochemical properties of **PTPTTBT-P1** and **PTPTTBT-P2** were investigated by cyclic voltammetry (CV) analysis. The CV experiments were conducted on a drop-cast polymer film on a platinum working electrode in acetonitrile (ACN) containing 0.1 M tetrabutylammonium tetrafluoroborate (TBATFB) as the supporting electrolyte at room temperature and ambient atmosphere at a scan rate of 100 mV/s. Ag/AgCl and platinum wire were used as the reference and counter electrodes, respectively. The performance of the CV instrument was calibrated using the ferrocene/ferrocenium (FOC) redox couple as an external standard before and after the analysis. The CV curves for **PTPTTBT-P1** and **PTPTTBT-P2** are shown in Fig. 3. The HOMO–LUMO levels of the polymers were calculated according to the following equation [20]: $E_{\text{HOMO}} = [-(E_{\text{ox,onset vs. Ag/AgCl}} - E_{\text{onset, ferrocene vs. Ag/AgCl}}) - 4.8]\text{eV}$ and $E_{\text{LUMO}} = [-(E_{\text{red, onset vs. Ag/AgCl}} - E_{\text{onset, ferrocene vs. Ag/AgCl}} - 4.8)]\text{eV}$, where 4.8 eV is the energy level of ferrocene below the vacuum level and $E_{\text{onset}}$ (ferrocene vs. Ag/AgCl) is 0.51 eV. The onset

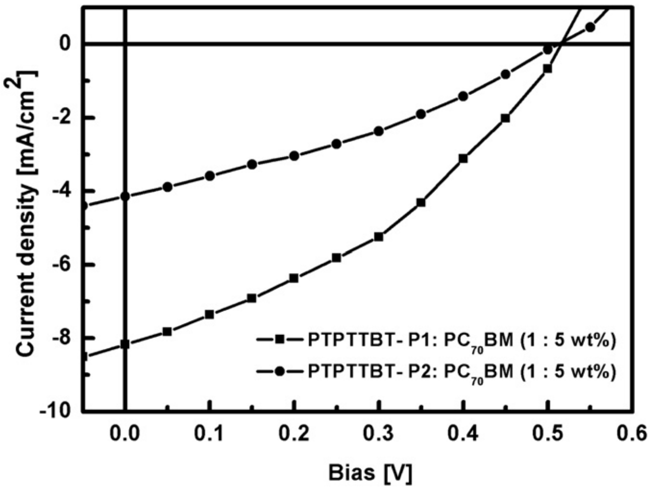


**Fig. 5.** *J*–*V* characteristics of BHJ solar cells prepared from ITO/PEDOT:PSS/**PTPTTBT-P1** (or) **PTPTTBT-P2**:PC$_{70}$BM (1:5 wt%)/TiO$_x$/Al under AM 1.5 irradiation (100 mW/cm$^2$).

oxidation potentials ($E_{ox,onset}$) of polymers **PTPTTBT-P1** and **PTPTTBT-P2** were determined to be 1.10 eV and 1.02 eV, respectively, and the highest occupied molecular orbital (HOMO) energy levels of **PTPTTBT-P1** and **PTPTTBT-P2** were calculated to be −5.39 eV and −5.31 eV, respectively. The lowest unoccupied molecular orbital (LUMO) energy levels of **PTPTTBT-P1** and **PTPTTBT-P2** were calculated to be −3.51 eV and −3.44 eV, respectively, from the onset reduction potentials ($E_{red,onset}$ −0.78 V and −0.85 V, respectively). The electrochemical band gaps calculated from the HOMO–LUMO levels of polymers **PTPTTBT-P1** and **PTPTTBT-P2** were 1.88 eV and 1.87 eV, respectively. The resulting electrochemical band gap (1.88 eV) of polymer **PTPTTBT-P1** is slightly lower than the optical band gap (1.94 eV) calculated from the onset of absorption. The electrochemical band gap (1.87 eV) of polymer **PTPTTBT-P2** is identical to the optical band gap (1.87 eV) calculated from the onset wavelength (664 nm) of the absorption at 522 nm. From the CV analysis, it is concluded that we can ignore the weak absorption at 832 nm for the optical band gap calculation for polymer **PTPTTBT-P2**. The electrochemical properties of the polymers are included in Table 1.

The HOMO and LUMO energy levels of the polymers are compared to those of PC$_{70}$BM and other materials used in BHJ solar cell fabrication in Fig. 4. The LUMO levels of the polymers are higher than that of PC$_{70}$BM and the differences between the LUMO levels of the polymers and PC$_{70}$BM are 0.79 eV and 0.86 eV, respectively. Consequently, the electron transfer from the polymers (electron donor) to PC$_{70}$BM (electron acceptor), which is the essential process for the charge separation of the excitons, can be allowed. In addition, the HOMO levels of the polymers are located quite below the LUMO level of PC$_{70}$BM and their energy differences are 1.09 eV and 1.01 eV, respectively. The energy difference between the HOMO level of the electron donor and the LUMO level of the electron acceptor has been known to be related to the open circuit voltage ($V_{oc}$) [36]. In this instance, copolymers **PTPTTBT-P1** and **PTPTTBT-P2**, which have the quite low HOMO levels, can induce reasonable $V_{oc}$ when they are used as electron donor materials in BHJ solar cells.

**Table 2**
Solar cell performance of **PTPTTBT-P1** and **PTPTTBT-P2** as electron donor with PC$_{70}$BM as an electron acceptor in ITO/PEDOT:PSS/**PTPTTBT-P1** (or) **PTPTTBT-P2**:PC$_{70}$BM (1:5 wt%)/TiO$_x$/Al device.

| Polymer | $V_{oc}$ (V)[a] | $J_{sc}$ (mA/cm$^2$)[b] | FF (%)[c] | PCE (%)[d] |
|---|---|---|---|---|
| **PTPTTBT-P1** | 0.52 | 8.17 | 36 | 1.57 |
| **PTPTTBT-P2** | 0.51 | 4.15 | 34 | 0.71 |

[a] Open-circuit voltage.
[b] Short-circuit current density.
[c] Fill factor.
[d] Power conversion efficiency.

### 3.4. BHJ solar cell properties

The photovoltaic properties of **PTPTTBT-P1** and **PTPTTBT-P2** were investigated by using the solution processable BHJ solar cells. To prepare the active layer, PC$_{70}$BM was used as an electron acceptor instead of PC$_{60}$BM because PC$_{70}$BM has similar electronic properties, but has the enhanced solar flux absorption at the high-energy part of the solar spectrum compared to PC$_{60}$BM [40]. The BHJ solar cell was fabricated with the configuration of ITO/PEDOT:PSS/**PTPTTBT-P1** (or) **PTPTTBT-P2**:PC$_{70}$BM/TiO$_x$/Al, where poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) was used to facilitate hole extraction and titanium oxide (TiO$_x$) was used for hole blocking as well as electron extraction purposes. In our previous studies, high PCEs were observed when the ratio of polymer:PC$_{70}$BM was 1:5 wt% in the active layer [29,30]. Consequently, in this study, the ratio of **PTPTTBT-P1**:PC$_{70}$BM or **PTPTTBT-P2**:PC$_{70}$BM was also set at 1:5 wt%.

Fig. 5 shows the typical current density–voltage (*J*–*V*) curves of the solar cell devices made from the blend of **PTPTTBT-P1** or

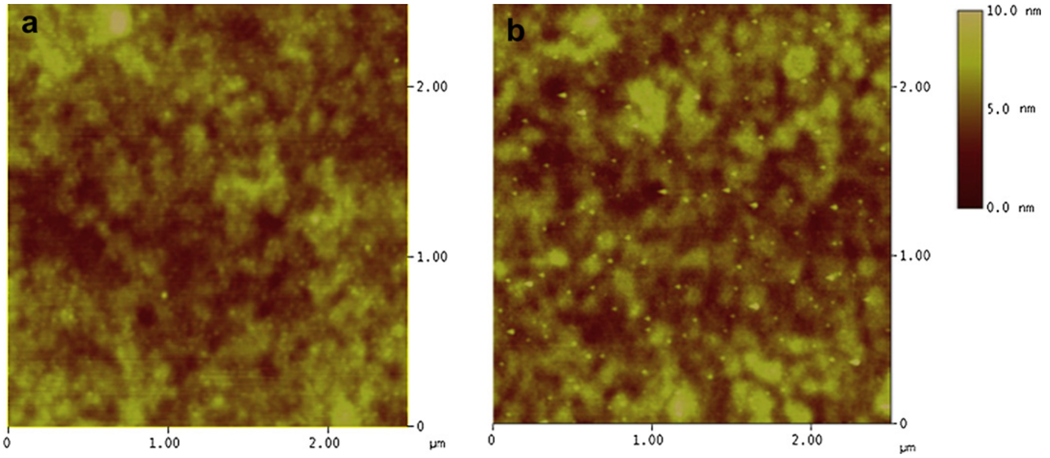


**Fig. 6.** AFM images obtained by tapping-mode on the surface for **PTPTTBT-P1**:PC$_{70}$BM (1:4 wt%) (a) and **PTPTTBT-P2**:PC$_{70}$BM (1:5 wt%) (b) spin coated thin film.

**PTPTTBT-P2** as the electron donor and $PC_{70}BM$ as the electron acceptor measured under the AM 1.5 G irradiation (100 mW/cm$^2$) from a solar simulator and the photovoltaic properties are summarized in Table 2. The device made from **PTPTTBT-P1**:$PC_{70}BM$ as the active layer shows the PCE of 1.57% with a short-circuit current density ($J_{sc}$) of 8.17 mA/cm$^2$, a $V_{oc}$ of 0.52 V, and a fill factor (FF) of 36% while that made from **PTPTTBT-P2**:$PC_{70}BM$ as the active layer shows the PCE of 0.71% with a $J_{sc}$ of 4.15 mA/cm$^2$, a $V_{oc}$ of 0.51 V, and an FF of 34%. The two devices show quite similar $V_{oc}$ and FF values. However, $J_{sc}$ value of the device made from **PTPTTBT-P1**:$PC_{70}BM$ is greater almost twice than that of the device made from **PTPTTBT-P2**:$PC_{70}BM$. These results indicate that the relatively high PCE of the device made from **PTPTTBT-P1**:$PC_{70}BM$ is concluded to rely on the relatively high $J_{sc}$. The higher $J_{sc}$ value observed on the device made from **PTPTTBT-P1**:$PC_{70}BM$ compared to that observed on the device made from **PTPTTBT-P2**:$PC_{70}BM$ under the identical experimental conditions is expected to be originated from the broad and flat absorption of polymer **PTPTTBT-P1**. In addition, the higher absorption intensity of **PTPTTBT-P1** compared to **PTPTTBT-P2** is expected to be also responsible for the higher $J_{sc}$ value observed on the device made from **PTPTTBT-P1**:$PC_{70}BM$.

The surface morphology of the active layers, which is quite important to the photovoltaic performance [41], was investigated by using AFM. The AFM images of the active layers of **PTPTTBT-P1**:$PC_{70}BM$ (1:5 wt%) and **PTPTTBT-P2**:$PC_{70}BM$ (1:5 wt%) are shown in Fig. 6. The root-mean-square (rms) roughness of the active layers was found to be 1.07 nm and 1.15 nm, respectively. This result indicates that the active layer surfaces are quite smooth and the two components of the active layers are homogeneously blended within the nanoscale. The slightly smoother surface of the active layer of **PTPTTBT-P1**:$PC_{70}BM$ compared to that of the active layer of **PTPTTBT-P2**:$PC_{70}BM$ might be also responsible for the higher $J_{sc}$ value observed on the device made from **PTPTTBT-P1**:$PC_{70}BM$.

## 4. Conclusions

In this study, two new alternating copolymers, **PTPTTBT-P1** and **PTPTTBT-P2**, incorporating electron rich TPT unit and electron deficient TBT unit were synthesized via the Suzuki polycondensation with reasonable yields. Polymer **PTPTTBT-P1** was found to show broad and flat absorption maximum. In addition polymer **PTPTTBT-P1** was found to show the higher absorption intensity compared to polymer **PTPTTBT-P2.** The BHJ solar cell device fabricated in ITO/PEDOT:PSS/**PTPTTBT-P1**:$PC_{70}BM$(1:5 wt%)/TiOx/Al configuration was found to give the PCE of 1.57%, while the device fabricated in ITO/PEDOT:PSS/**PTPTTBT-P2**:$PC_{70}BM$(1:5 wt%)/TiOx/Al configuration was found to give the PCE of 0.71%. The higher PCE of the device made from the blend of **PTPTTBT-P1** and $PC_{70}BM$ as an active layer was found to rely on the relatively high $J_{sc}$ value. The relatively high $J_{sc}$ value of the active layer of **PTPTTBT-P1**:$PC_{70}BM$ was proposed to be originated from the broad and flat absorption and the high absorption intensity of **PTPTTBT-P1**. The slightly smoother surface of the active layer of **PTPTTBT-P1**:$PC_{70}BM$ compared to that of the active layer of **PTPTTBT-P2**:$PC_{70}BM$ might be also responsible for the higher $J_{sc}$ value observed on the device made from **PTPTTBT-P1**:$PC_{70}BM$. We hope that the optimization of the device preparation condition or the modification of the device architecture would considerably enhance the PCEs.

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