

A Novel Donor-Acceptor-Acceptor-Acceptor Polymer Containing Benzodithiophene and Benzimidazole-Benzothiadiazole-Benzimidazole for PSCs

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New electron deficient acceptor-acceptor-acceptor type of monomer unit composed of weak electron accepting benzimidazole and relatively strong electron accepting benzothiadiazole derivatives namely 4,7-bis(6-bromo-1-(2-ethylhexyl)-1*H*-benzo[*d*]imidazol-2-yl)benzo[*c*][1,2,5]thiadiazole (BBB) was synthesized. The Stille polycondensation of the newly synthesized BBB monomer with electron donating 2,6-bis(trimethyltin)-4,8-bis(2-ethylhexyloxy)benzo[1,2-*b*:4,5-*b'*]dithiophene (BDT) afforded donor-acceptor-acceptor-acceptor type of polymer namely 2,6-(4,8-bis(2-ethylhexyloxy)benzo[1,2-*b*:4,5-*b'*]dithiophene)-alt-4,7-bis(1-(2-ethylhexyl)-1*H*-benzo[*d*]imidazol-2-yl)benzo[*c*][1,2,5]thiadiazole (**PBDTBBB**). The opto-electrical studies revealed that the absorption band of **PBDTBBB** appeared in the range of 300 nm-525 nm and its highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels were positioned at -5.18 eV and -2.84 eV, respectively. The power conversion efficiency (*PCE*) of the polymer solar cell (PSC) prepared from **PBDTBBB**:PC₇₁BM (1:2 wt %) blend was 1.90%.

Key Words : Donor-acceptor polymer, Benzodithiophene, Benzimidazole, Benzothiadiazole

Introduction

Polymer based bulk heterojunction solar cells (PSCs) have been considered as one of the most promising green energy production techniques.¹ For the past few years, various efforts have been focused on the enhancement of the power conversion efficiency (*PCE*) of PSCs. The efforts include, for example, replacing the large band gap most successful electron donating poly(3-hexylthiophene) (P3HT) with structurally new low band gap polymers which harvest the sun light quite efficiently along with high carrier mobility,² replacing the common electron accepting PC₆₀BM or PC₇₁BM with new electron acceptor (ICMA and ICBA etc...) derivatives which show higher LUMO levels and better absorptions than PC₆₀BM,³ tuning the PSCs device structure to inverted or tandem structure according to the merits of the electron donor or acceptor materials properties,⁴⁻⁷ and inserting new electron transporting or hole transporting buffer layers at the various junctions of the PSCs to improve the electron and hole separation.^{8,9} Especially, developing structurally new π -conjugated polymers for PSCs has attracted a great attention at institution as well as industry because the electron donating polymers used to construct the photoactive layer of the PSCs play important roles in determining the device performances of PSCs.

In this instance, developing structurally new polymers which show broad absorption band (effective light harvesting leads high current density), appropriate energy levels (deep HOMO and higher LUMO levels are expected to offer

high open circuit voltage and better charge dissociation) and high carrier mobility (high fill factor) is still challenging. The simple and efficient way to prepare broad absorbing polymer is to copolymerize the electron rich and electron deficient moiety in alternate fashion. It is well known that the 2,1,3-benzothiadiazole (BT)-based electron deficient units are quite much efficient in preparing highly efficient polymers showing broad absorption band in entire visible part of the solar spectrum and the maximum *PCE* of 8.2% and 10.6% was obtained for the BT-based polymers in single layer and tandem PSCs, respectively.¹⁰⁻¹⁵ In order to tune the opto-electrical properties of BT-based polymers numerous electron rich and some electron accepting units have been incorporated or inserted onto the BT moiety and various BT-based acceptor units were developed (see Figure 1 for the examples of BT-based acceptor units).^{13,15-22} We have also interested in the development of BT-based acceptor units by incorporating a weak electron accepting unit on the both side of strong electron accepting BT unit to evaluate opto-electrical and photovoltaic properties of the polymers containing weak and strong electron acceptor unit in their main chain. We expect that *N*-alkylbenzimidazole is the favorable choice as a weak electron accepting unit since the electron donating benzene ring is fused with electron accepting imidazole ring. In addition, the *N*-alkyl group on benzimidazole ring is expected to increase the solubility of new acceptor-acceptor-acceptor (A-A-A) type of monomer as well as the final polymers, which is also crucial for the solution processability. Here, we report the detailed synthesis of a novel donor-acceptor-acceptor-acceptor polymer (**PBDTBBB**) incorporating a new BT-based A-A-A type of monomer and the

²These authors contributed equally to this work.

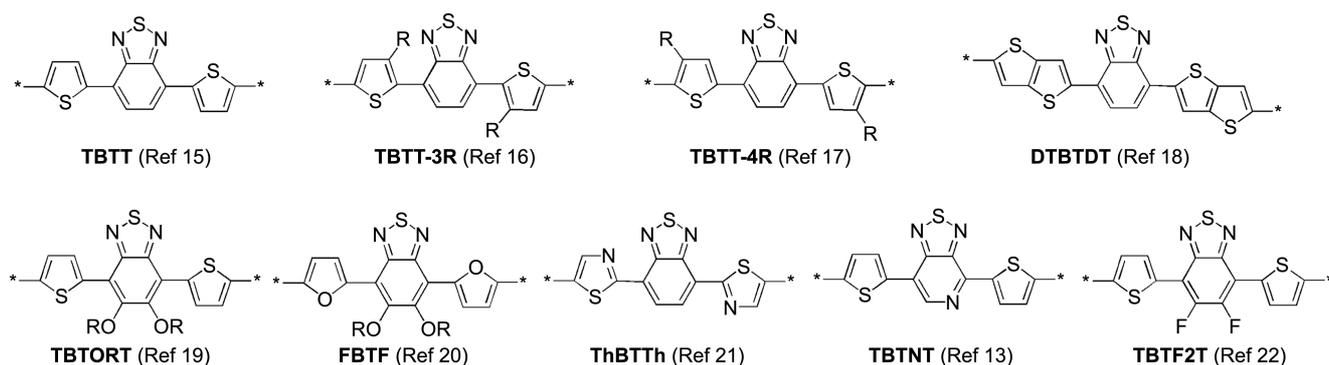


Figure 1. Examples of benzothiadiazole (BT)-based acceptor units.

optical, electrochemical and photovoltaic properties of the polymer.

Experimental

Materials and Instruments. The necessary reagents and solvents were received from Aldrich or TCI chemicals and used without further purification. The column chromatography was performed on silica gel (Merck Kieselgel 60, 70-230 mesh ASTM). The proton (^1H) and carbon (^{13}C) nuclear magnetic resonance (NMR) spectra of the newly synthesized compounds were recorded on Varian Mercury Plus spectrometer (300 MHz and 75 MHz, respectively). The weight molecular weight (M_w) and polydispersity (PDI) of the polymer was analyzed by Gel permeation chromatography (GPC) on Agilent 1200 Infinity Series separation module using polystyrene as a standard and chloroform as an eluent. Thermogravimetric analysis (TGA) was conducted with a TA instrument Q500 at a heating rate of 10 $^\circ\text{C}/\text{min}$ under nitrogen. The absorption spectra of the polymer in chloroform and as thin film on glass were recorded on JASCO V-570 spectrophotometer. The cyclic voltammetry (CV) measurements were performed using a CH Instruments Electrochemical Analyzer with three electrode system made up with Ag/AgCl as a reference electrode, platinum as a working and counter electrode in a 0.1 M tetrabutylammonium tetrafluoroborate (Bu_4NBF_4) chloroform solution as the supporting electrolyte at room temperature.

PSCs Fabrication and Characterization. ITO-coated glass substrates were cleaned and PEDOT:PSS (Clevious P, 50 nm) was spin-coated on top of ITO substrate at 5000 rpm for 30 s and dried at 150 $^\circ\text{C}$ for 10 min under vacuum. Then, the **PBDTBBB** and PC_{71}BM blend (1:1 wt % or 1:2 wt % or 1:3 wt %) was spin-coated on top of ITO/PEDOT:PSS substrate from a dichlorobenzene (DCB) solution at 1000 rpm. The ITO/PEDOT:PSS/**PBDTBBB**: PC_{71}BM substrate was heated at 80 $^\circ\text{C}$ for 20 min in a glove box to remove residual solvents. The corresponding active layer thickness was estimated to be around 80 nm. The ITO/PEDOT:PSS/**PBDTBBB**: PC_{71}BM substrate was transferred to the vacuum chamber and an approximately 0.7 nm thick LiF layer was deposited on the substrate. Subsequently, a 100 nm thick Al layer was deposited through a shadow mask on top of the

ITO/PEDOT:PSS/**PBDTBBB**: PC_{71}BM /LiF substrate under a high vacuum (3.0×10^{-6} torr). The top metal electrode area, comprising the active area of the solar cell, was found to be 0.36 cm^2 . The J - V characteristics of the devices were measured using a Keithley 2400 source measure unit under a calibrated AM 1.5G solar simulator (Pecell Technologies Inc., PEC-L11) at 100 mW/cm^2 . The intensity of sunlight illumination was calibrated using a standard Si photodiode detector with a KG-5 filter. The film thickness was measured using a KLA Tencor Alpha-step IQ surface profilometer with an accuracy of ± 1 nm.

Synthesis of 4,7-Bis(bromomethyl)benzo[*c*][1,2,5]thiadiazole (1). To the stirred solution of 2,1,3-benzothiadiazole (2 g, 14.7 mmol) in 48% aqueous hydrobromic acid (HBr, 40 mL) and glacial acetic acid (10 mL) were added trioxane (1.62 g, 73.5 mmol) and trimethyl(tetradecyl)ammonium bromide (0.30 g) at room temperature (RT). The solution was refluxed for 24 h. After cooling, the solid was filtered and washed with water and ethanol and then dried under vacuum to afford compound **1** as an off-white solid. Yield: (3.00 g, 63%). ^1H NMR (300 MHz, CDCl_3) δ 7.63 (s, 2 H), 4.97 (d, 4 H); ^{13}C NMR (75 MHz, CDCl_3) δ 153.8, 131.5, 129.6, 28.3; HRMS (EI^+ , m/z) [M^+] Calcd for $\text{C}_8\text{H}_6\text{Br}_2\text{N}_2\text{S}$ 319.8618, found 319.8622.

Synthesis of Benzo[*c*][1,2,5]thiadiazole-4,7-dicarbaldehyde (2). Compound **1** (3.00 g, 9.30 mmol) and sodium periodate (NaIO_4) (0.99 g, 4.8 mmol) were taken in a round bottom flask under argon atmosphere. The above mixture was dissolved in 30 mL of *N,N*-dimethylformamide (DMF) and then slowly heated to 150 $^\circ\text{C}$ with stirring. The progress of the reaction was monitored by thin layer chromatography (TLC) by comparison with the starting material (hexane:ethyl acetate (EA), 9:1 v/v). The starting material was completely disappeared within 60 min and two new spots were found by TLC. Solvent was completely removed by rotary evaporation and then the solid material was poured into 50 mL of water. The mixture was stirred for 30 min at RT and then extracted with EA for three times (30 mL \times 3). The combined organic layer was washed with brine and dried over anhydrous Na_2SO_4 . The solution was filtered and evaporated by rotary evaporation and the crude product was purified by column chromatography (silica gel, hexane:EA, 9:1 v/v) to afford pure compound **2** as an orange solid. Yield: (0.60 g, 34%). ^1H

NMR (300 MHz, CDCl₃) δ 10.90 (s, 2 H), 8.39 (s, 2 H); ¹³C NMR (75 MHz, CDCl₃) δ 188.7, 154.1, 131.1, 130.6; HRMS (EI⁺, *m/z*) [M⁺] Calcd for C₈H₄N₂O₂S 191.9993, found 191.9996.

Synthesis of 4,7-Bis(6-bromo-1*H*-benzo[*d*]imidazol-2-yl)benzo[*c*][1,2,5]thiadiazole (3). Compound **3** was synthesized *via* the method similar to the reported procedure.²³ The solution of 4-bromobenzene-1,2-diamine (1.07 g, 5.75 mmol) in 10 mL of dimethylacetamide (DMAc) was taken in a two neck round bottom flask (50 mL) under argon atmosphere. The solution was cooled to -15 °C for 15 min. by using a bath containing ice and acetone, then compound **2** (0.50 g, 2.60 mmol) in 20 mL of DMAc was added drop by drop to the stirred solution at -15 °C. The solution was stirred on the same bath for 4 h and then the bath was removed and stirred at RT for 6 h. The solution was then poured into a 250 mL beaker and 0.005 g of iron(III) chloride (FeCl₃) was added and the mixture was stirred for 12 h at ambient atmosphere. The stirring was stopped and the mixture was kept to stand for 1 h at RT. Finally the mixture was filtered and the solid material was washed well with chloroform (CHCl₃) to afford compound **3** as a red solid. Yield: (1.00 g, 73%). ¹H NMR (300 MHz, DMSO-*d*₆) δ 8.80 (s, 2H), 7.93 (s, 2 H), 7.70 (d, 2 H), 7.39 (d, 2 H).

Synthesis of 4,7-Bis(6-bromo-1-(2-ethylhexyl)-1*H*-benzo[*d*]imidazol-2-yl)benzo[*c*][1,2,5]thiadiazole (BBB): To a stirred solution of compound **3** (0.60 g, 1.15 mmol) in anhydrous DMF (50 mL) was added sodium carbonate (0.80 g, 5.75 mmol) and stirring was continued for 15 min at RT. Then, 2-ethylhexyl bromide (1.00 mL, 5.75 mmol) was added and stirred at 70 °C for 24 h. DMF was completely removed by rotary evaporation and then the sticky mass was dissolved in EA (50 mL). The organic solution was washed with brine and dried over anhydrous Na₂SO₄. The solution was filtered and evaporated by rotary evaporation and the crude product was purified by column chromatography (silica gel, hexane:EA, 90/10) to afford pure monomer BBB as a brown color solid. Yield: (0.36 g, 42%). ¹H NMR (300 MHz, CDCl₃) δ 8.16 (s, 2 H), 8.05 (s, 2 H), 7.50 (d, 2 H), 7.38 (d, 2 H), 4.19 (d, 4 H), 1.58-1.76 (m, 2 H), 0.90-1.20 (m, 16 H), 0.72 (t, 6 H), 0.58 (t, 6 H); ¹³C NMR (75 MHz, CDCl₃) δ 153.1, 150.8, 144.8, 135.1, 132.0, 126.7, 126.3, 123.5, 115.9, 112.2, 49.6, 39.5, 30.7, 28.6, 23.9, 23.0, 14.1, 10.7; HRMS (EI⁺, *m/z*) [M⁺] Calcd for C₃₆H₄₂Br₂N₆S 748.1558, found 751.1619.

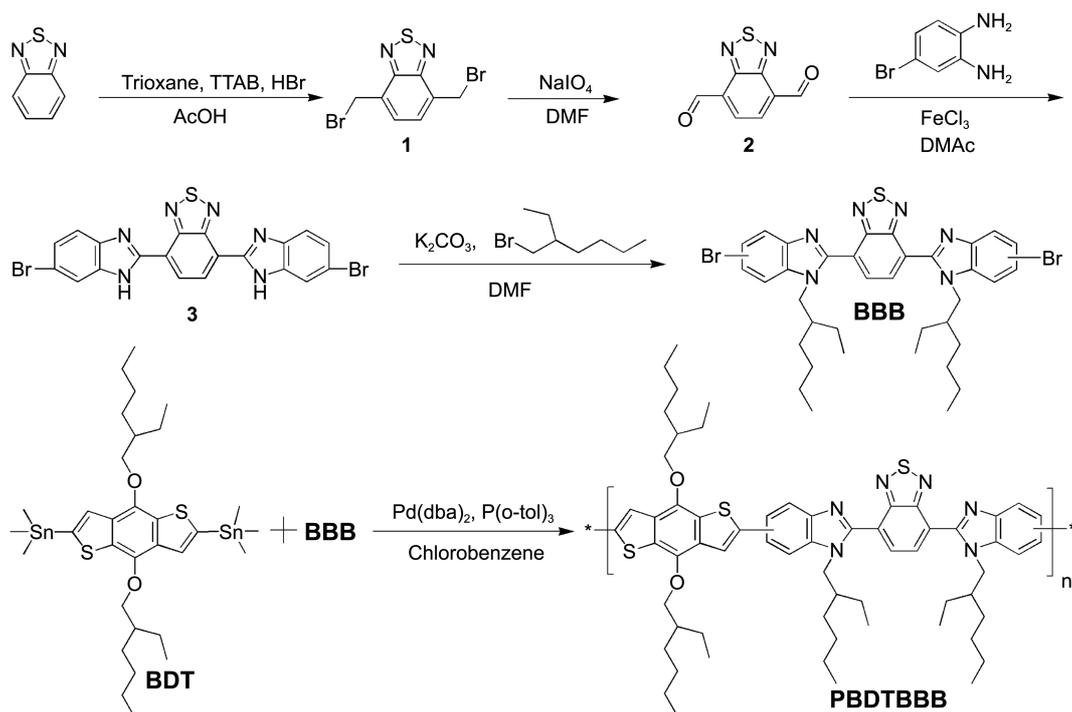
Synthesis of 2,6-(4,8-Bis(2-ethylhexyloxy)benzo[1,2-*b*:4,5-*b'*]dithiophene)-*alt*-4,7-bis(1-(2-ethylhexyl)-1*H*-benzo[*d*]imidazol-2-yl)benzo[*c*][1,2,5]thiadiazole (PBDTBBB). A solution of monomers BDT (0.19 g, 0.25 mmol) and BBB (0.19 g, 0.25 mmol) in chlorobenzene (15 mL) was purged well with argon for 45 min. Then, Pd₂dba₃Cl₂ (0.02 g) and P(*o*-tolyl)₃ (0.05 g) were added to the stirred solution and the mixture was heated to reflux for 48 h under argon atmosphere. Then, the solution was cooled to RT and added drop wise to the vigorously stirred methanol (100 mL). After stirring for 30 min, the mixture was kept to stand for 1 h at RT. The precipitate was filtered and washed with 2 N HCl

and acetone. The crude polymer was purified by Soxhlet extraction with methanol for 24 h and acetone for 24 h to offer polymer **PBDTBBB** as a brown color solid. Yield: (0.12 g, 46%). ¹H NMR (300 MHz, CDCl₃) δ 8.20-8.36 (m, 2 H), 7.40-7.90 (m, 8 H), 4.27 (s, 8 H), 1.30-2.00 (m, 20 H), 0.80-1.20 (m, 28 H), 0.75 (s, 6 H), 0.62 (s, 6 H).

Results and Discussion

The synthetic procedures for the structurally new benzimidazole-benzothiadiazole-benzimidazole monomer unit and polymer **PBDTBBB** are outlined in Scheme 1. The synthetic procedures for compounds **1** and **2** have been reported.^{24,25} However, compounds **1** and **2** were prepared more efficiently *via* the methods shown in Scheme 1 than the methods reported. 2,1,3-Benzothiadiazole was treated with trioxane in 48% HBr and acetic acid to afford 4,7-bis(bromomethyl)benzo[*c*][1,2,5]thiadiazole (**1**). The oxidation of compound **1** by using NaIO₄ yielded benzo[*c*][1,2,5]thiadiazole-4,7-dicarbaldehyde (**2**). The condensation followed by the cyclization of compound **2** with 4-bromobenzene-1,2-diamine in presence of iron (III) chloride afforded 4,7-bis(6-bromo-1*H*-benzo[*d*]imidazol-2-yl)benzo[*c*][1,2,5]thiadiazole (**3**). Even though only one structure is presented in Scheme 1, it should be noted that compound **3** can have three isomers due to the N-H hydrogen exchange between 1,3-positions of the imidazole ring without considering the conformational isomers resulted from the rotation around the C-C bond between the aromatic rings. However, the ¹H NMR spectrum for compound **3** was found to show only one symmetrical structure, indicating the fast equilibrium between imidazole tautomers. *N*-Alkylation of compound **3** by treating with K₂CO₃ and 2-ethylhexyl bromide gave structurally new acceptor-acceptor-acceptor type of monomer BBB. The structure of monomer BBB expected from the ¹H and ¹³C NMR spectra is symmetrical. Consequently, the two *N*-alkyl groups should be in the same side. In addition, in order to avoid the steric hindrance with the thiadiazole ring, the two *N*-alkyl groups might be positioned to the opposite side of the thiadiazole ring. However, the bromide group can be placed at 5- or 6-position of the benzimidazole ring. The isomers originated from the bromide position were not identified and, consequently, the exact position of the bromide group was not indicated in the structure of monomer BBB shown in Scheme 1.

The Stille polymerization between the monomers BDT and BBB followed by the Soxhlet purification offered polymer **PBDTBBB**. The solubility of the polymer was tested in common organic solvents such as chloroform, chlorobenzene and dichlorobenzene. Polymer **PBDTBBB** showed good solubility in chlorobenzene and dichlorobenzene and moderate solubility in chloroform at ambient temperature. The chemical structure of the polymer was confirmed by NMR and GPC analysis. The GPC analysis revealed that the weight average molecular weight (*M_w*) and polydispersity (PDI) of polymer **PBDTBBB** were 1.41 × 10⁴ g and 1.82, respectively. In order to estimate the thermal stability of



Scheme 1. Synthetic route for the synthesis of polymer **PBDTBBB**.

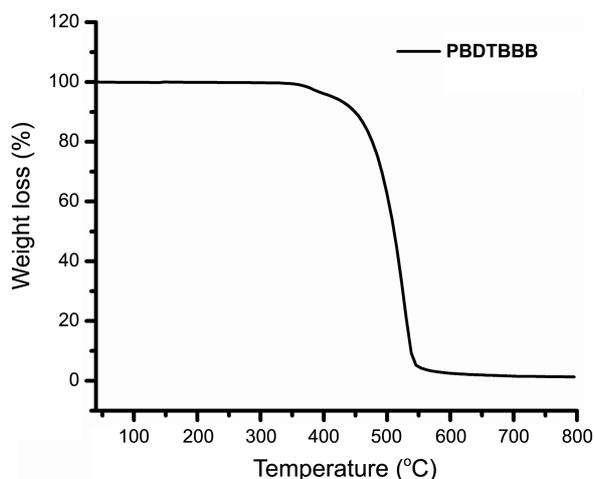


Figure 2. TGA curves of **PBDTBBB**.

polymer **PBDTBBB**, the thermogravimetric analysis (TGA) was performed and the corresponding TGA curve is presented in Figure 2. From the TGA analysis, the 5% weight loss temperature of polymer **PBDTBBB** was estimated to be 415 °C. The high degradation temperature allowed polymer **PBDTBBB** to optoelectronic applications.

The absorption spectra of polymer **PBDTBBB** shown in Figure 3 were measured in a chloroform solution and as thin film on glass. The absorption band of **PBDTBBB** was found to be quite similar in both solution and film state and it was found to cover the range of 300 nm–525 nm with maximum absorption at 387 nm in chloroform and 376 nm as thin film on glass. The absorption band of **PBDTBBB** is expected to be originated from π – π^* electronic transitions. Usually, BT-

based donor-acceptor-donor (D-A-D) polymers shows two absorption band originated from π – π^* electronic transitions (\sim 300–500 nm) and internal charge transfer (ICT) (\sim 500–800 nm).^{10–15} However, the newly synthesized D-A-A-A polymer (**PBDTBBB**) exhibited only π – π^* electronic transitions and the absorption resulted from ICT was found to be completely absent. It is well known that the ICT mainly depends on the planarity of the repeating units of polymer. We expect that the presence of sterically hindered 2-ethylhexyl groups on the polymer back bone might diminish the planarity, and consequently, ICT completely diminished. Interestingly, the absorption bands of the polymers incorporating TBTT, TBTT-3R, TBTT-4R or TBTORT (see Figure 1) units found to be red shifted in the order of TBTT > TBTORT > TBTT-4R > TBTT-3R.^{15,17,19,26–28} The planarity of the TBTT unit decreased significantly when the alkyl groups were introduced on their back bone and consequently showed blue shifted absorption band.^{24–26} In this instance, we expect that controlling the position and/or the length of the alkyl group on the BBB unit of the polymer might offer more red shifted absorption compared to that of **PBDTBBB**. The absorption maximum of **PBDTBBB** in film state was found to be blue shifted by 9 nm compared to that in solution state, which indicates the π – π stacking or π – π interaction of **PBDTBBB** is reduced in film state due to the large steric hindrance. The optical band gap (E_g) of **PBDTBBB** was calculated from the onset wavelength of the optical absorption as thin film to be 2.34 eV. The optical property of **PBDTBBB** is summarized in Table 1.

The PL measurement of polymer **PBDTBBB** was carried out in chloroform and as thin film with excitation at 385 nm and 375 nm, respectively. The PL spectra are displayed in

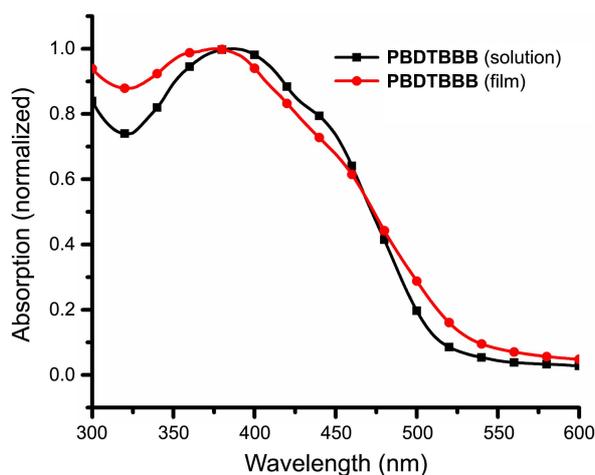


Figure 3. Absorption spectra of PBDTBBB.

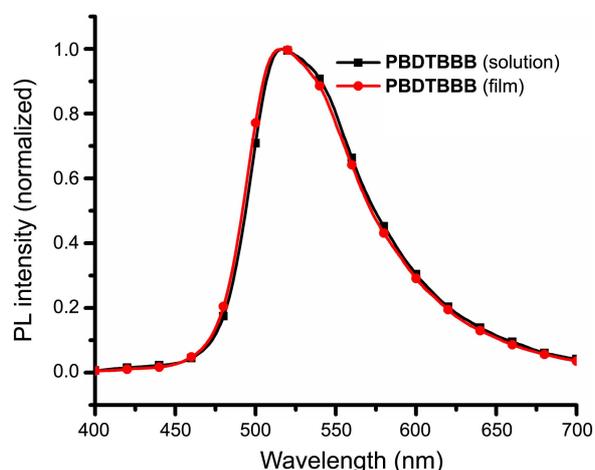


Figure 4. Photoluminescence spectra of PBDTBBB.

Figure 4. The PL spectra of polymer PBDTBBB were found to be almost identical both in solution and as thin film with the PL bands in the region of 450–650 nm. The PL maximum values are listed in Table 1.

To evaluate the electro-chemical properties of PBDTBBB, we performed cyclic voltammetry (CV) analysis with polymer PBDTBBB. The CV measurement was carried out in 0.1 M tetrabutylammonium tetrafluoroborate (Bu_4NBF_4) chloroform solution with three electrodes such as Ag/AgCl as a reference electrode, platinum as a working and counter electrode at room temperature. The CV spectrum of PBDTBBB is presented in Figure 5. The onset oxidation potential ($E_{\text{ox,onset}}$) of PBDTBBB was estimated to be 0.78 V

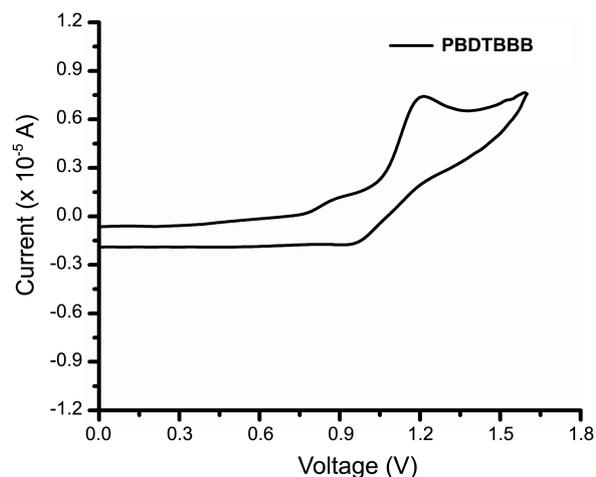


Figure 5. Cyclic voltammogram of PBDTBBB.

from the CV curve shown in Figure 5. The HOMO energy level of the polymer was determined to be -5.18 eV by using the known equation of $E_{\text{HOMO}} = -(E_{\text{ox,onset}} + 4.4)$ eV.^{21,22} On the other hand, the LUMO energy level of PBDTBBB was calculated to be -2.84 eV from HOMO energy level and optical band gap values by using the equation $\text{LUMO} = \text{HOMO} + E_{\text{g}}$.^{29,30} The HOMO and LUMO levels of PBDTBBB indicate that its HOMO energy level is deep enough to get reasonable V_{oc} and the LUMO level is positioned well above the LUMO level of the acceptor (PC_{71}BM), which ensures the possibility of the efficient electron transfer from the polymer to PC_{71}BM .^{31,32} In this instance, the synthesized polymer PBDTBBB might be suitable for PSCs application. The HOMO and LUMO energy levels of PBDTBBB were included in Table 1.

To investigate the energy conversion efficiency of polymer PBDTBBB, we fabricated the PSC device with the structure of ITO/PEDOT:PSS/PBDTBBB: PC_{71}BM (1:1 wt % or 1:2 wt % or 1:3 wt %)/LiF/Al. The current density-voltage (J - V) characteristics of the PSC devices were measured under the illumination of AM 1.5 G ($100 \text{ mW}/\text{cm}^2$) solar simulator. The J - V curves are shown in Figure 6 and the corresponding photovoltaic parameters were presented in Table 2. The PSC made with PBDTBBB: PC_{71}BM (1:2 wt %) blend as an active layer offered maximum PCE of 1.90% with an open circuit voltage (V_{oc}) of 0.64 V, a current density (J_{sc}) of 5.80 mA/cm^2 , and fill factor (FF) of 51%. On the contrary, the PSCs prepared with PBDTBBB: PC_{71}BM (1:1 wt %) and PBDTBBB: PC_{71}BM (1:3 wt %) blends as an active layer showed decreased PCE of 1.21% ($V_{\text{oc}} = 0.65$ V, $J_{\text{sc}} = 5.46$

Table 1. Summary of the optical and electrochemical properties of PBDTBBB

Polymer	$\lambda_{\text{max, soln}}$ (nm) ^a	$\lambda_{\text{max, Film}}$ (nm) ^b	$E_{\text{g, opt}}$ (eV) ^c	$\text{PL}_{\text{max, soln}}$ (nm) ^d	$\text{PL}_{\text{max, film}}$ (nm) ^e	HOMO (eV) ^f	LUMO (eV) ^g
PBDTBBB	387	376	2.34	518	516	-5.18	-2.84

^aAbsorption maximum of the polymer in chloroform solution. ^bAbsorption maximum of the polymer as thin film onto the glass substrate. ^cThe optical band gap estimated from the onset wavelength of the optical absorption in thin film. ^dPhotoluminescence maximum of the polymer in chloroform solution. ^ePhotoluminescence maximum of the polymer as thin film onto the glass substrate. ^fThe HOMO level of the polymer estimated from cyclic voltammetry analysis. ^gThe LUMO level of the polymer calculated by using the equation of $\text{LUMO} = \text{HOMO} + E_{\text{g}}$.

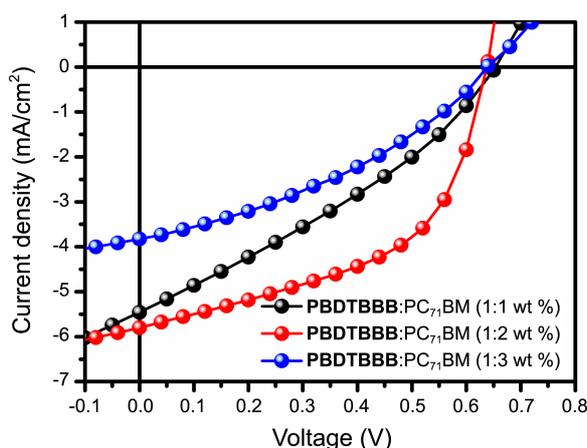


Figure 6. J - V curves for the PSCs prepared from **PBDTBBB**.

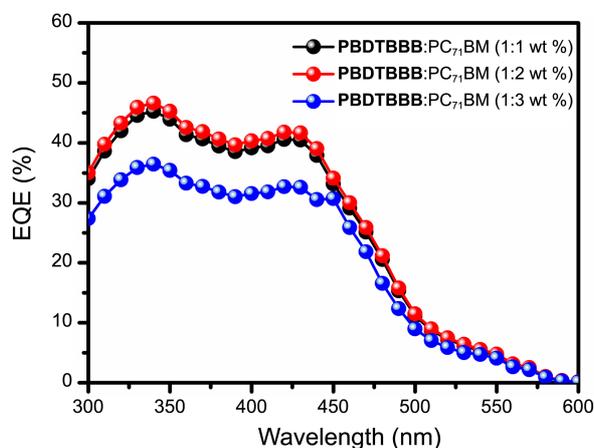


Figure 7. EQE spectra for the PSCs prepared from **PBDTBBB**.

mA/cm^2 and $FF = 34\%$) and 0.89% ($V_{oc} = 0.64$ V, $J_{sc} = 3.83$ mA/cm^2 and $FF = 36\%$), respectively, compared to that of the PSC made from **PBDTBBB**: PC_{71}BM (1:2 wt %).

Figure 7 display the EQE (External Quantum Efficiency) spectra of the PSCs fabricated with three different donor: acceptor blends such as 1:1 wt %, 1:2 wt % and 1:3 wt %. The EQE curves for the PSCs are found to cover the region from 300 nm to 550 nm. The PSC prepared from **PBDTBBB**: PC_{71}BM (1:2 wt %) blend exhibited higher EQE response than that of the PSC prepared from **PBDTBBB**: PC_{71}BM (1:1 wt %) or **PBDTBBB**: PC_{71}BM (1:3 wt %) blend. The

Table 2. Photovoltaic properties of **PBDTBBB**

PBDTBBB : PC_{71}BM	V_{oc} (V) ^a	J_{sc} (mA/cm^2) ^b	FF (%) ^c	PCE (%) ^d
1:1 wt %	0.65	5.46	34	1.21
1:2 wt %	0.64	5.80	51	1.90
1:3 wt %	0.64	3.83	36	0.89

^aOpen circuit voltage. ^bCurrent density. ^cFill factor. ^dPower conversion efficiency.

maximum EQE values of the PSCs fabricated with **PBDTBBB**: PC_{71}BM (1:1 wt %) and **PBDTBBB**: PC_{71}BM (1:2 wt %) blends were more than 45 % while the PSC prepared with **PBDTBBB**: PC_{71}BM (1:3 wt %) displayed decreased EQE maximum value ($\sim 35\%$).

The surface morphologies of **PBDTBBB**: PC_{71}BM blends (1:1 wt %, 1:2 wt % and 1:3 wt %) were investigated by using AFM. The AFM images of **PBDTBBB**: PC_{71}BM blends are shown in Figure 8. The root-mean-square (rms) roughness of the three blends was estimated to be 1.2 nm, 0.7 nm and 3.0 nm, respectively. The AFM images suggest that the two components such as **PBDTBBB** and PC_{71}BM are homogeneously blended for 1:1 wt % and 1:2 wt % blends while some aggregation of PC_{71}BM was observed for 1:3 wt % blend. The relatively smoother surface and homogeneous blending between the donor and acceptor for 1:2 wt % blend offered higher J_{sc} and PCE values than those of 1:1 wt % and 1:3 wt % blends.

Conclusion

Preparation of new monomer unit (BBB) composed of weak electron accepting benzimidazole and relatively strong electron accepting benzothiadiazole derivatives was reported. To evaluate the potentials of BBB unit, we copolymerized it with BDT to afford new polymer **PBDTBBB**. The absorption band of **PBDTBBB** was found to cover the region from 300 nm to 500 nm and the energy levels were found to be suitable for application to PSCs. The PSC (ITO/PEDOT:PSS/active layer/LiF/Al) prepared from the active layer of **PBDTBBB**: PC_{71}BM (1:2 wt %) gave maximum PCE of 1.90%. Even though the PCE obtained in this study is not so high, we expect that optimizing the structure of BBB unit might offer highly efficient polymer for PSCs.

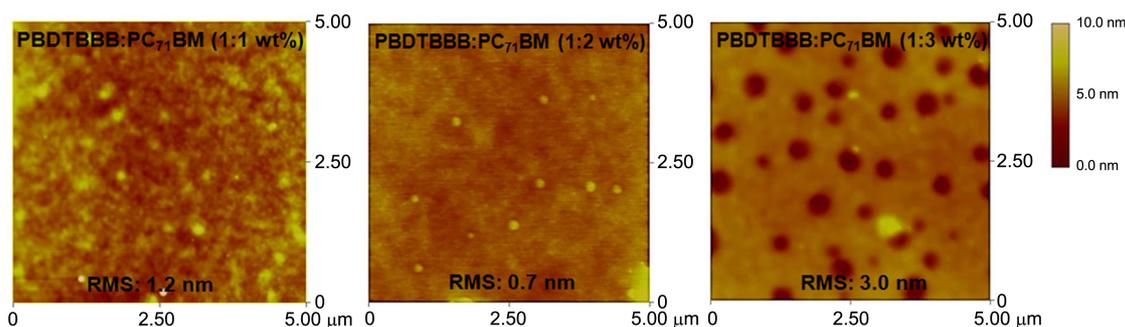


Figure 8. AFM images of **PBDTBBB**: PC_{71}BM (1:1 wt %), **PBDTBBB**: PC_{71}BM (1:2 wt %) and **PBDTBBB**: PC_{71}BM (1:3 wt %) blends.

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References

1. Søndergaard, R.; Hösel, M.; Angmo, D.; Larsen-Olsen, T. T.; Krebs, F. C. *Mater Today* **2012**, *15*, 36.
2. Li, Y. *Acc. Chem. Res.* **2012**, *45*, 723.
3. He, Y.; Chen, H.-Y.; Hou, J.; Li, Y. *J. Am. Chem. Soc.* **2010**, *132*, 1377.
4. You, J.; Chen, C.-C.; Hong, Z.; Yoshimura, K.; Ohya, K.; Xu, R.; Ye, S.; Gao, J.; Li, G.; Yang, Y. *Adv. Mater.* **2013**, *25*, 3973.
5. Li, W.; Furlan, A.; Hendriks, K. H.; Wienk, M. M.; Janssen, R. A. *J. Am. Chem. Soc.* **2013**, *135*, 5529.
6. Chen, S.; Small, C. E.; Amb, C. M.; Subbiah, J.; Lai, T.; Tsang, S.-W.; Manders, J. R.; Reynolds, J. R.; So, F. *Adv. Energy Mater.* **2012**, *2*, 1333.
7. Small, C. E.; Chen, S.; Subbiah, J.; Amb, C. M.; Tsang, S.-W.; Lai, T.-H.; Reynolds, J. R.; So, F. *Nat. Photon.* **2012**, *6*, 115.
8. Po, R.; Carbonera, C.; Bernardia, A.; Camaioni, N. *Energy Environ. Sci.* **2011**, *4*, 285.
9. Lunt, R. R.; Osedach, T. P.; Brown, P. R.; Rowehl, J. A.; Bulovic, V. *Adv. Mater.* **2011**, *23*, 5712.
10. You, J.; Dou, L.; Yoshimura, K.; Kato, T.; Ohya, K.; Moriarty, T.; Emery, K.; Chen, C.-C.; Gao, J.; Li, G.; Yang, Y. *Nat. Commun.* **2013**, doi: 10.1038/ncomms2411.
11. Osaka, I.; Kakara, T.; Takemura, N.; Koganezawa, T.; Takimiya, K. *J. Am. Chem. Soc.* **2013**, *135*, 8834.
12. Stuart, A. C.; Tumbleston, J. R.; Zhou, H.; Li, W.; Liu, S.; Ade, H.; You, W. *J. Am. Chem. Soc.* **2013**, *135*, 1806.
13. Zhou, H.; Yang, L.; Stuart, A. C.; Price, S. C.; Liu, S.; You, W. *Angew. Chem. Int. Ed.* **2011**, *50*, 2995.
14. He, Z.; Zhong, C.; Huang, X.; Wong, W.-Y.; Wu, H.; Chen, L.; Su, S.; Cao, Y. *Adv. Mater.* **2011**, *23*, 4636.
15. Park, S. H.; Roy, A.; Beaupre, S.; Cho, S.; Coates, N.; Moon, J. S.; Moses, D.; Leclerc, M.; Lee, K.; Heeger, A. J. *Nat. Photon.* **2009**, *3*, 297.
16. Biniek, L.; Chochos, C. L.; Leclerc, N.; Hadziioannou, G.; Kallitsis, J. K.; Bechara, R.; Leveque, P.; Heiser, T. *J. Mater. Chem.* **2009**, *19*, 4946.
17. Qua, B.; Yanga, H.; Tianb, D.; Liub, H.; Congb, Z.; Gaob, C.; Chena, Z.; Xiaoa, L.; Gaoa, Z.; Weic, W.; Gongga, Q. *Syn. Metals* **2012**, *162*, 2020.
18. Xia, Y.; He, Z.; Tong, J.; Li, B.; Wang, C.; Cao, Y.; Wu, H.; Woo, H. Y.; Fan, D. *Macromol. Chem. Phys.* **2011**, *212*, 1193.
19. Almeataq, M. S.; Yi, H.; Al-Faifi, S.; Alghamdi, A. A. B.; Iraqi, A.; Scarratt, N. W.; Wang, T.; Lidzey, D. G. *Chem. Commun.* **2013**, *49*, 2252.
20. Wang, X.; Chen, S.; Sun, Y.; Zhang, M.; Li, Y.; Li, X.; Wang, H. *Polym. Chem.* **2011**, *2*, 2872.
21. Cao, Y.; Lei, T.; Yuan, J.; Wang, J.-Y.; Pei, J. *Polym. Chem.* **2013**, *4*, 5228.
22. Zhou, H.; Yang, L.; Price, S. C.; Knight, K. J.; You, W. *Angew. Chem. Int. Ed.* **2010**, *49*, 7992.
23. Zhu, H.; Tong, H.; Gong, Y.; Shao, S.; Deng, C.; Yuan, W. Z.; Zhang, Z. *Polym. Sci. Part A: Polym. Chem.* **2012**, *50*, 2172.
24. Yamamoto, T.; Adachi, T.; Sugimoto, M. *ACS Macro. Lett.* **2013**, *2*, 7903.
25. Pesin, V. G.; Dyachenko, E. K. *Khimiya Geterotsiklicheskikh Soedinenii* **1967**, *6*, 1048.
26. Biniek, L.; Chochos, C. L.; Hadziioannou, G.; Leclerc, N.; Leveque, P.; Heiser, T. *Macromol. Rapid Commun.* **2010**, *31*, 651.
27. Tamilavan, V.; Song, M.; Kim, S.; Agneeswari, R.; Kang, J.-W.; Hyun, M. H. *Polymer* **2013**, *54*, 3198.
28. Tamilavan, V.; Song, M.; Jin, S.-H.; Hyun, M. H. *Polymer* **2011**, *52*, 2384.
29. Tamilavan, V.; Sakthivel, P.; Li, Y.; Song, M.; Kim, C.-H.; Jin, S.-H.; Hyun, M. H. *J. Polym. Sci. Part A: Polym. Chem.* **2010**, *48*, 3169.
30. Tamilavan, V.; Song, M.; Jin, S.-H.; Hyun, M. H. *J. Polym. Sci. Part A: Polym. Chem.* **2010**, *48*, 5514.
31. Tamilavan, V.; Song, M.; Agneeswari, R.; Kang, J.-W.; Hwang, D.-H.; Hyun, M. H. *Polymer* **2013**, *54*, 6125.
32. Tamilavan, V.; Song, M.; Jin, S.-H.; Hyun, M. H. *Curr. Appl. Phys.* **2012**, *12*, S124.