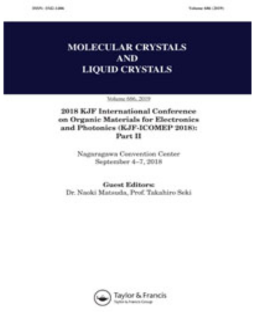
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Synthesis of a new wide-bandgap conjugated copolymer with 3-trifluoromethylthiophene monomer and Its application to non-fullerene polymer solar cells

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ABSTRACT
In this study, a novel wide-bandgap conjugate donor-acceptor type copolymer, **PBDT-TFMTh**, containing benzodithiophene (BDT) as a donor unit and trifluoromethyl (TFM)-substituted thiophene (Th) as an acceptor unit was designed and synthesized. The physical, optical, and electrochemical properties of **PBDT-TFMTh** were studied in detail and it was found to have lower-lying highest occupied and lowest unoccupied molecular orbitals. The polymer solar cell with an active layer consisting of **PBDT-TFMTh** and acceptor IDT(TCV)$_2$ showed a relatively high power conversion efficiency of 2.25% after thermal annealing at 120 °C.

KEYWORDS
3-trifluoromethylthiophene; wide-bandgap copolymer; polymer solar cell; power conversion efficiency

Introduction

Over the last decade, the synthesis and application of thiophene-based oligomers or polymers to materials science have been of great interest because of their desirable functional attributes in organic solar cells [1,2] and organic field effect transistors [3,4]. In recent years, thiophene-based polymers have attracted significant attention and have been extensively incorporated into polymer solar cells (PSCs) because of their low-cost device fabrication, light weight, and flexible chemical structure [5].

It has been previously demonstrated that the preparation of the active layer in bulk heterojunction (BHJ) type PSCs is based primarily on a blend of polymer electron donors and small organic acceptor molecules or polymer electron acceptors. The power conversion efficiency (PCE) of a BHJ-PSC device is directly proportional to the short-circuit current density (J_{sc}), open-circuit voltage (V_{oc}), and fill factor (*FF*). Since V_{oc} is mainly determined by the difference between the highest occupied molecular orbital (HOMO) of a donor and the lowest unoccupied molecular orbital (LUMO) of an acceptor, the exploration of a conjugated polymer with a low-lying HOMO energy level is a feasible approach to increase V_{oc}. In general, the HOMO energy level of the donor polymer can be significantly lowered by reducing the effective conjugation length to inhibit the delocalization of π-electrons in the

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polymer backbone. For example, the HOMO level of a copolymer prepared by using a fluorene monomer tends to be low [6].

An alternative method for lowering the HOMO energy level of a polythiophene derivative is by copolymerization of the thiophene monomer with an electron-withdrawing substituent. Some research groups have reported polythiophene-containing thiophene-3-carboxylate electron-withdrawing monomers [7,8]. In addition, polythiophenes with cyano [9] and fluorine [10,11] electron-withdrawing substituents in the main chain reportedly have a relatively low-lying HOMO level.

Thus, it may be quite advantageous to synthesize a conjugated copolymer by replacing an electron donor monomer with an electron-withdrawing monomer and utilize the corresponding copolymer to fabricate a BHJ-type PSC. For example, Liang et al. introduced a fluorine atom into the TT unit of the PBDTTs, and the HOMO level of the polymer was altered such that the corresponding PSC demonstrated a higher V_{oc} [12]. Apart from the fluoro substituent, CF_3 units have often been used to adjust the electronic structure of small organic molecules. However, to the best of our knowledge, there is no report on the synthesis of donor-acceptor (D–A) type copolymers containing a CF_3-substituted thiophene monomer and its use as a polymer donor in the fabrication of BHJ-type PSCs.

In this work, for the first time, we report a new D–A type conjugated copolymer **PBDT-TFMTh**, which contains a trifluoromethyl (TFM)-substituted thiophene (Th) monomer and a benzodithiophene (BDT) unit. Compared to **PBDT-Th**, the polymer bearing neat thiophene as the monomer, it was evident that replacing the thiophene unit with the TFM-substituted thiophene unit in the polymer backbone structure led to lowering of the HOMO and LUMO energy levels of **PBDT-TFMTh** (Scheme 1). The PSC made of **PBDT-TFMTh:**IDT(TCV)$_2$ showed a relatively high PCE of 2.25% after thermal annealing at 120 °C.

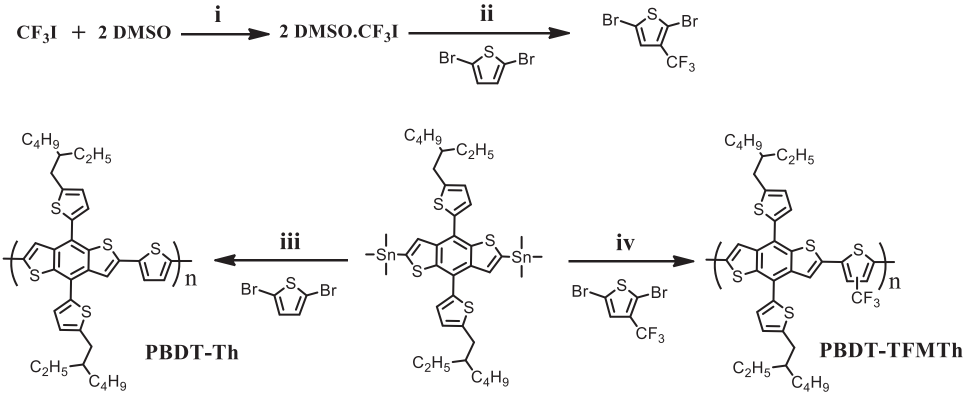
Experimental details

Materials

2,5-Dibromo-3-(trifluoromethyl)thiophene and (4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-*b*:4,5-*b*']dithiophene-2,6-diyl)bis(trimethylstannane) were prepared according to literature methods [8,13–15].

Instrumentation

The absorption spectra of the polymer were recorded using a UV – Vis absorption spectrometer (Agilent 8453, PDA type, $\lambda = 190 - 1100$ nm). The electrochemical properties were characterized by cyclic voltammetry (CV, eDAQ EA161) with an electrolyte solution containing tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) in acetonitrile. A platinum wire and Ag/AgCl (3M NaCl) were purchased from BASi Corporation and used as the counter and reference electrodes, respectively. Elemental analyses were performed using an EA1112 (Thermo Electron Corp.) elemental analyzer. The molecular weights of the synthesized polymers were measured relative to polystyrene (PS) standards by gel permeation chromatography (GPC) with chlorobenzene at 85 °C as an eluent using an Agilent GPC 1200 series instrument. The surface morphologies of the



Scheme 1. Synthetic pathway of 3-trifluoromethylthiophene and copolymers **PBDT-Th** and **PBDT-TFMTh**. (i) -78 °C; (ii) $K_2S_2O_8$, $Cu(OAc)_2{\cdot}H_2O$, 90 °C, 24 h; (iii) $Pd_2(dba)_3$, P(*o*-tolyl)$_3$, toluene, 120 °C, 24 h; (iv) $Pd_2(dba)_3$, P(*o*-tolyl)$_3$, toluene, 120 °C, 48 h.

polymer films were investigated using an atomic force microscope (AFM, XE-100, Advanced Scanning Probe Microscope, PSIA) with a silicon cantilever.

Synthesis of PBDT-TFMTh

(4,8-Bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-*b*:4,5-*b*']dithiophene-2,6-diyl)bis(trimethyl stannane) (0.045 g, 0.05 mmol), 2,5-dibromo-3-(trifluoromethyl)thiophene (0.015 g, 0.05 mmol), tris(dibenzylideneacetone)dipalladium(0) (2.0 mg, 5.0 mol%), tri(*o*-tolyl)phosphine (1.5 mg, 10 mol%), and anhydrous toluene (5.0 mL) were added to a Schlenk tube. The reaction mixture was then stirred at 120 °C for 48 h. After precipitation in MeOH, the crude polymer was filtered and dried under vacuum. The precipitate was purified by Soxhlet extraction using methanol, acetone, hexane, and chloroform sequentially. The resultant polymer was collected, dried under vacuum, and obtained as a red solid in 69% yield (25 mg). GPC: M_n = 15.4 kg/mol, PDI = 1.76. Anal. calcd for $(C_{39}H_{41}F_3S_5)_n$: C, 64.43; H, 5.68; S, 22.05. Found: C, 64.37; H, 5.65; S, 21.94.

Synthesis of PBDT-Th

PBDT-Th was synthesized using (4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-*b*:4,5-*b*']dithiophene-2,6-diyl)bis(trimethyl stannane) (0.181 g, 0.2 mmol) and 2,5-dibromothiophene (0.048 g, 0.2 mmol) following the synthetic procedure outlined above for **PBDT-TFMTh**. Yield: 81.5% (106 mg). GPC: M_n = 8.8 kg/mol, PDI = 2.40. Anal. calcd for $(C_{38}H_{42}S_5)_n$: C, 69.25; H, 6.42; S, 24.33. Found: C, 69.21; H, 6.44; S, 24.27.

Results and discussion

Synthesis and characterization

In this work, we designed a new wide-bandgap conjugated copolymer (**PBDT-TFMTh**) containing BDT as a donor unit and 3-trifluoromethylthienyl (TFMTh) unit as an

Table 1. Physical, optical, and electrochemical parameters of **PBDT-TFMTh** and **PBDT-Th**.

			Absorption (nm)					Energy level (eV)	
Polymer	M_n (kg/mol)	PDI	solution	film	$\lambda_{\text{cut-off}}{}^{a}$ (nm)	$E_g{}^{\text{opt}b}$ (eV)	$E_{\text{ox}}{}^{c}$ (V)	HOMO^d	LUMO^e
PBDT-TFMTh	15.3	1.75	470	518	605	2.05	0.87	−5.77	−3.72
PBDT-Th	8.8	2.40	518	525	600	2.07	1.35	−5.29	−3.22

[a] Film
[b] Calculated from the onset of optical absorption
[c] Determined by CVs of thin films on the Pt electrode
[d] HOMO = $-(4.42 + E_{\text{ox}})$
[e] LUMO = HOMO + $E_g{}^{\text{opt}}$.

acceptor unit, and synthesized it by Stille coupling polymerization. A heteroacene-type donor, BDT was employed as a building block with a long alkyl-chain substituent that imparted a high degree of planarity and better solubility. In addition, we introduced the electron-withdrawing TFM-substituted thiophene monomer into the polymer backbone to modulate the HOMO and LUMO levels.

The monomer, trifluoromethylated dibromothiophene, was synthesized by trifluoromethylation of dibromothiophene using freshly prepared dimethyl sulfoxide (DMSO)·CF_3I adduct, potassium persulfate, and Cu medium in DMSO as solvent according to the literature procedure [13,14]. Additionally, **PBDT-Th** as a control copolymer was prepared as shown in Scheme 1. The number average molecular weights (M_n) and polydispersity indices (PDI) of the obtained polymers, **PBDT-TFMTh** and **PBDT-Th**, were 15.4 and 8.8 kg/mol, and 1.76 and 2.4, respectively (Table 1).

Optical and electrochemical properties

The UV-Vis absorption spectra of the conjugated copolymer **PBDT-TFMTh** in solution and thin film states is shown in Figure 1. The corresponding parameters are summarized in Table 1. As shown in Figures 1a and 1b, the maximum absorption wavelength in the solution and film states were observed respectively at 470 and 518 nm for **PBDT-TFMTh**, and 418 and 525 nm for **PBDT-Th** as the control polymer. Compared to **PBDT-Th**, **PBDT-TFMTh** showed blue-shifted absorption spectrum which is due to highly twisted structure with a large dihedral angle between BDT and TFMTh. Interestingly, the absorption spectrum of the **PBDT-TFMTh** film was red-shifted compared to that of **PBDT-Th**, which may be attributed to the strong interactions between the polymer chains in the solid state. The optical bandgap of the copolymer **PBDT-TFMTh** was estimated to be 2.05 eV from the onset wavelength ($\lambda_{\text{cut-off}} = 605$ nm) of the absorption spectrum of the thin film (Table 1). Thus, the copolymer having **TFMTh** could be classified as a wide-bandgap polymer applicable to a non-fullerene PSC that effectively induced complementary absorption when mixed with a low bandgap acceptor to produce an active layer, as shown in Figure 1c.

We performed CV to investigate the electrochemical properties of the copolymers **PBDT-Th** and **PBDT-TFMTh** in their thin film states, and the corresponding parameters are shown in Table 1. The HOMO levels of the copolymers were estimated using the onset oxidation potentials (E_{ox}s). As shown in Figure 2a, the values of E_{ox} were 0.87 and 1.35 V for **PBDT-Th** and **PBDT-TFMTh**, respectively. The estimated HOMO energy levels of **PBDT-Th** and **PBDT-TFMTh** were then calculated as −5.29 and

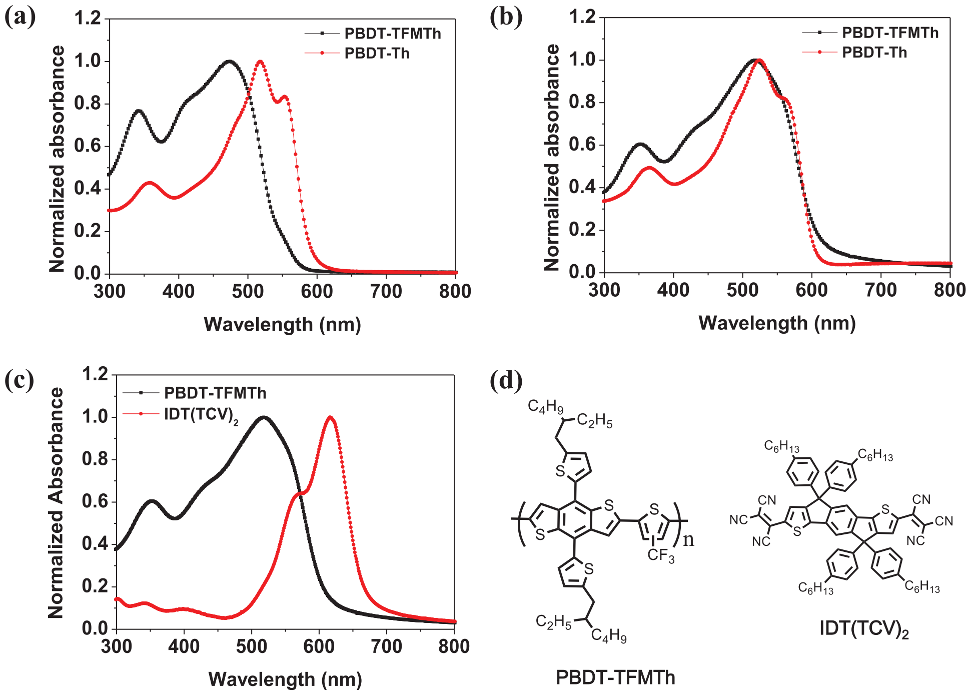


Figure 1. UV-Vis absorption spectra of **PBDT-TFMTh** and **PBDT-Th** in solution (a) and thin film states (b). UV-Vis absorption spectra of **PBDT-TFMTh** as the donor polymer and IDT(TCV)$_2$ in film states. (c) Molecular structures of **PBDT-TFMTh** donor and IDT(TCV)$_2$ acceptor.

−5.77 eV, respectively. The electron-withdrawing TFM unit in **PBDT-TFMTh** resulted in a lower-lying HOMO energy level compared to that of **PBDT-Th**. The LUMO energy levels were −3.22 and −3.72 eV for **PBDT-Th** and **PBDT-TFMTh**, respectively.

Non-fullerene polymer solar cells

The photovoltaic properties of the blend films bearing copolymer **PBDT-TFMTh** as the donor and IDT(TCV)$_2$ as the non-fullerene acceptor were investigated in an inverted device configuration. The polymer solar cells used in this study were fabricated according to a previously reported method [8]. The active layers were obtained by spin coating the chlorobenzene solution (2 wt %) of the polymers (PBDT-TFMTh or PBDT-Th) and IDT(TCV)$_2$ with different weight ratio. The LUMO and HOMO energy levels of the selected acceptor matched well with those of the copolymer **PBDT-TFMTh**. To obtain the best PSC performance, the active layer thickness and the blending ratio of the donor and acceptor were precisely optimized. The effect of varying blend compositions on PSC performance parameters is presented in Table 2.

The current-voltage (*J*-*V*) and EQE curves of the optimized devices with the blend film as the active layer are shown in Figures 3a and 3b. Among the as-cast active layers with the same composition, the highest efficiency was obtained when the weight ratio of **PBDT-TFMTh** to IDT(TCV)$_2$ was 2:1. The PSC prepared using the **PBDT-TFMTh**:IDT(TCV)$_2$ (weight ratio = 2: 1) blend film showed 1.96% PCE (V_{oc} of 0.71 V, J_{sc} of 6.54 mA cm^{-2}, and FF of 42.34%). We also conducted the thermal annealing of

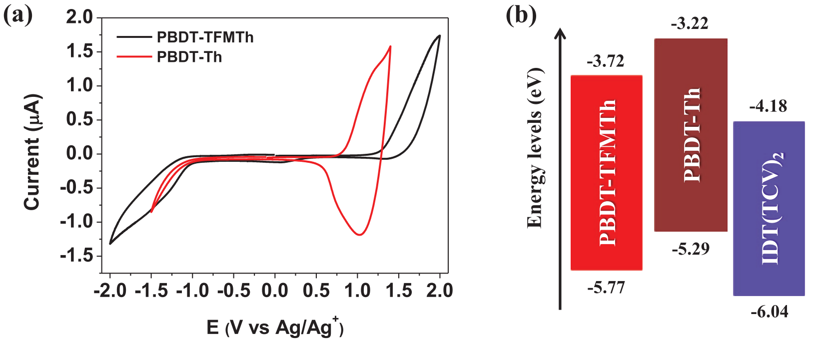


Figure 2. (a) Cyclic voltammograms of the thin films of **PBDT-Th** and **PBDT-TFMTh**. (b) Energy diagram of **PBDT-Th** and **PBDT-TFMTh** as donors and IDT(TCV)$_2$ as an acceptor.

Table 2. Parameters of PSCs fabricated using **PBDT-TFMTh**:IDT(TCV)$_2$ and **PBDT-Th**:IDT(TCV)$_2$

Donor	Acceptor	D/A ratio (w/w%)	Annealing temp. (°C)	V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)	PCE (%)
PBDT-TFMTh	IDT(TCV)$_2$	1:1	–	0.70	6.25	44.39	1.95
		1:1	100	0.69	6.09	49.99	2.08
		1:1/CN[a]	–	0.71	6.02	48.73	2.07
		2:1	–	0.71	6.54	42.34	1.98
		2:1	120	0.69	6.44	50.14	2.25
		1:2	–	0.71	4.64	42.23	1.39
PBDT-Th	IDT(TCV)$_2$	2:1	120	0.31	2.53	46.20	0.37

[a] 1-Chloronaphthalene (CN) was used as a solvent additive.

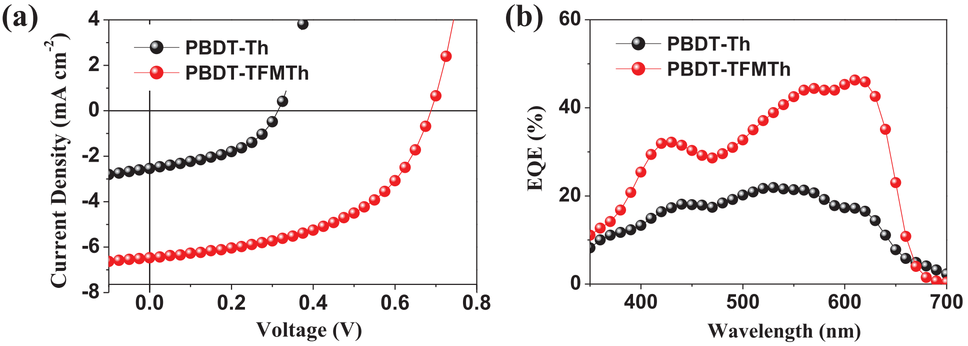


Figure 3. *J-V* curve of the PSC device based on **PBDT-Th**:IDT(TCV)$_2$ and **PBDT-TFMTh**:IDT(TCV)$_2$ blend films (2:1) annealed at 120 °C (a) and corresponding EQE curves (b).

the active layer at different temperatures. This resulted in slightly increasing the FF values of the different PSCs and their PCE values also increased from 1.96 to 2.25% (Table 2). The EQE spectra of the PSCs were recorded in the range of 320 to 700 nm. The maximum EQE value of the PSC based on **PBDT-TFMTh**:IDT(TCV)$_2$ (2:1 wt%) was observed at 610 nm. Thus, according to the preliminary experimental results, the copolymer **PBDT-TFMTh** is a promising donor material for PSC devices.

It is well-known that the internal morphology of donor-acceptor blend films has a significant effect on the performances of BHJ-type PSC devices [16]. The surface morphology of the active layer in the PSC device was measured by atomic force microscopy (AFM). The AFM height images are displayed in Figure 4. It was found that the

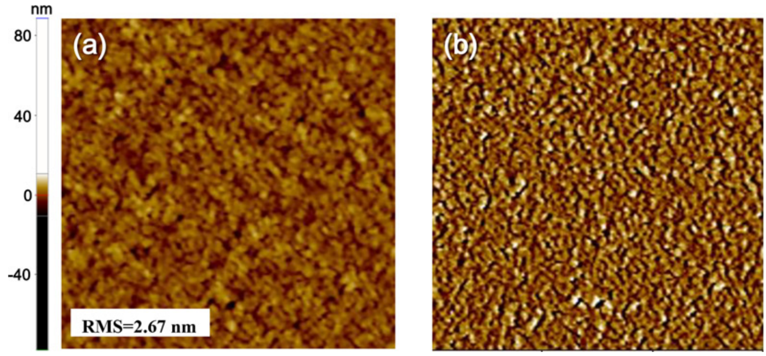


Figure 4. AFM height (a) and phase (b) images (3 × 3 μm) of the **PBDT-TFMTh**:IDT(TCV)$_2$ (2:1 wt. ratio) blend.

high PSC device performance ($\eta = 2.25\%$) was observed when **PBDT-TFMTh** was blended with IDT(TCV)$_2$. This resulted in a fine surface morphology with a relatively small surface roughness of 2.67 nm. The small surface roughness was likely due to the fine internal morphology of the active layer so that efficient exciton diffusion and exciton dissociation/charge transport were expected.

Conclusion

We have successfully synthesized a new wide-bandgap conjugated copolymer, **PBDT-TFMTh**, having thiophene monomers substituted with a TFM group by Stille coupling polymerization. The introduction of the TFM group into the thiophene ring in **PBDT-TFMTh** effectively changed the HOMO and LUMO levels. The PSC fabricated using **PBDT-TFMTh** as the donor and IDT(TCV)$_2$ as the non-fullerene acceptor showed a maximum PCE of 2.25%, which was attributable to its fine blend morphology. The PCE of the **PBDT-TFMTh**-based PSC indicated that the introduction of the TFM substituent is a promising strategy to prepare wide-bandgap donor polymers for PSC applications.

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