

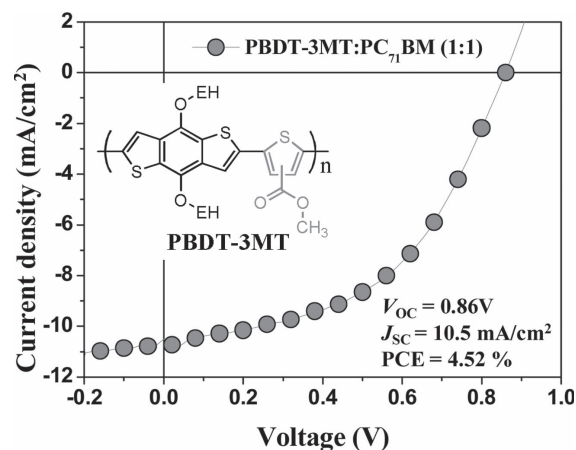
Enhanced Performance of Organic Photovoltaic Cells Fabricated with a Methyl Thiophene-3-Carboxylate-Containing Alternating Conjugated Copolymer

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A new donor-acceptor copolymer, containing benzodithiophene (BDT) and methyl thiophene-3-carboxylate (3MT) units, is designed and synthesized for polymer solar cells (PSCs). The 3MT unit is used as an electron acceptor unit in this copolymer to provide a lower highest occupied molecular orbital (HOMO) level for obtaining polymer solar cells with a higher open-circuit voltage (V_{OC}). The resulting bulk heterojunction PSC made of the copolymer and [6,6]-phenyl-C71-butyric acid methyl ester (PC₇₁BM) exhibits a power conversion efficiency (PCE) up to 4.52%, a short circuit current (J_{SC}) of 10.5 mA·cm⁻², and a V_{OC} of 0.86 V.

1. Introduction

Polymer solar cells (PSCs) have attracted much attention due to the low cost of device fabrication by using solution-processing technology, such as roll to roll, spin-coating, drop-casting and ink-jet printing etc. In particular, their mechanical flexibility offers potential feasibility for flexible photovoltaic (PV) devices.^[1–7] Bulk heterojunction (BHJ) PSCs, based on the blending of polymeric electron donors and fullerene-based soluble acceptors (PCBM), have become the most successful devices for organic photovoltaics (OPVs).^[8–11] In the past, several groups have optimized BHJ-type OPV device performance by using regioregular poly(3-hexylthiophene)(P3HT) and [6,6]-phenyl-C61-butyric acid methyl ester (PC₆₁BM). BHJ solar cells have already reached 4–6% of power conversion efficiency under illumination



of AM 1.5 solar irradiation (100 mW·cm⁻²).^[12–15] Although P3HT has been reported to exhibit very promising PSC performance, the efficiency of these solar cells is often limited by a low open circuit voltage (V_{OC}). V_{OC} is proportional to the energy gap between the highest occupied molecular orbital (HOMO) of the electron donating polymers and the lowest unoccupied molecular orbital (LUMO) of the electron accepting PCBM.^[16]

To obtain a lower HOMO energy level in electron donating polymers, some conjugated polymers composed of electron donating and electron withdrawing units, have been suggested in the literature. Some donor-acceptor (D-A) copolymers have been demonstrated to yield the high V_{OC} in PSCs by using fluorene derivatives as an electron donor. The fluorene derivatives are a well-known class of wide-band-gap semiconducting materials. Many examples of these copolymers have exhibited lower HOMO levels, resulting in a high V_{OC} of BHJ PSC with

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PC₆₁BM. However, these copolymers usually resulted in relatively lower PSCs efficiencies (~4%).^[17–19] Fortunately, a few polymers, containing different donating groups, were successfully shown to give higher V_{OC} (above 0.85 V) and PCE (above 5%). These polymers have been synthesized using 4,7-dithien-2-yl-2,1,3-benzothiadiazole (DTBT) as an electron acceptor and silafluorene,^[20] carbazole^[21] and benzodithiophene^[22] derivatives as an electron donors.

It is quite intriguing that alkyl thiophene-3-carboxylate (TC) groups behave as electron-withdrawing units into the main-chain of thiophene-based conjugated polymers. In the last case, poly (alkyl thiophene-3-carboxylates) derivatives were designed and synthesized by Pomerantz and Fréchet's groups.^[23–25] They demonstrated a new synthetic method for these polymers and their potential application in organic light emitting diodes (OLEDs) and organic thin film transistors (OTFTs). In 2009, Yang and Li's groups first reported highly improved device performances in PSC fabricated with poly (3-carboxylated thienylenevinylene) (P3CTV, see Scheme 1) and PC₆₁BM. 2.01% of PCE was obtained to be 10 times higher than that of poly (3-hexyl thienylenevinylene) (P3HTV) without carboxylate groups. The V_{OC} also successfully increased to 0.86 V from 0.54 V.^[26] In the same year, Kerbs and coworkers synthesized a new copolymer containing thermal-cleavable alkyl TC. The resulting polymer showed increased V_{OC} of 0.73 V in BHJ polymer solar cells.^[27,28] Recently, Hu et al. reported a new regiorandom PCTBDT which is an alternating copolymer made of benzodithiophene (BDT) and hexyl thiophene-3-carboxylate, as shown in the molecular structure of Scheme 1. The PSC based on the blends of PCTBDT and PCBM exhibited PCE up to 2.32% with V_{OC} of 0.80 V.^[29] Although PCTBDT exhibited an improved V_{OC} value by introducing long alkyl TC, the PCE value is still relatively low. It is useful to explore new molecular structures for showing much higher PCE without decreasing V_{OC} . The longer alkyl-substituted TC monomer of regiorandom copolymers could impede the ability to obtain the well-ordered interchain lamellar structure and good charge

carrier mobility.^[25] In this work, we designed and synthesized a new alternating D-A copolymer (PBDT-3MT) by using BDT derivative and methyl thiophene-3-carboxylate (3MT). By shortening the length of the side chain in TC monomer, we could anticipate an improvement of the interchain interaction between polymer chains, resulting in higher crystallinity and device efficiency in OPVs. The branched alkyl substituted BDT derivative as an electron donor monomer was selected to afford the solubility of the newly synthesized copolymer. The PBDT-3MT exhibited good solubility in common solvents and a deeper HOMO energy level only by reducing the length of the alkyl side chain in TC monomer. Particularly, as shown by optical absorption studies in the solution state, the PBDT-3MT showed stronger thermochromic behavior than the reported alkyl TC-based copolymers. Herein we describe the synthesis and characterization of the copolymer in detail and report on its performance when used as the active layer in BHJ polymer solar cells.

2. Experimental Section

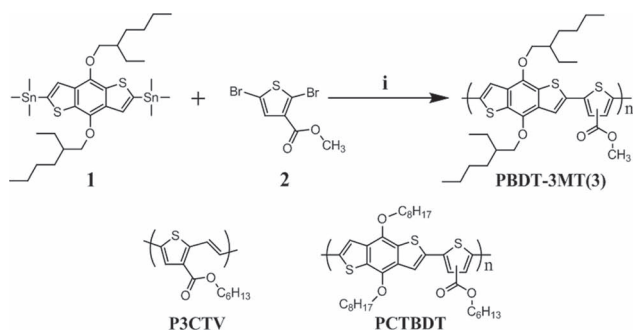
2.1. Materials

All reagents were purchased from Sigma-Aldrich Co. and used without further purification, unless stated otherwise. Reagent grade solvents used in this study were freshly dried under standard distillation methods. Monomers **1** and **2** were prepared according to published procedures.^[30,31] The copolymer PBDT-3MT was synthesized by the Stille coupling reaction, which is described in detail below.

Monomer **1** (0.26 g, 0.34×10^{-3} mol), monomer **2** (0.10 g, 0.34×10^{-3} mol), Pd(PPh₃)₄ (0.012 g, 0.01×10^{-3} mol) were dissolved in anhydrous toluene (18 mL) and dimethylformamide (DMF) (2 mL). The reaction mixture was heated to 110 °C and stirred for 60 h. The solution was precipitated into methanol (200 mL) and collected by filtration. The filtrate was subjected to Soxhlet extraction with acetone and chloroform. The polymer solution in chloroform was concentrated and slowly dropped into methanol. The pure polymer (0.15 g, 77%) was obtained as a dark red solid by filtration and drying under vacuum. ¹H NMR (400 MHz, CDCl₃, δ): 7.98 (br, 1H), 7.41–7.74 (br, 2H), 4.12 (br, 4H), 3.97 (br, 3H), 1.86 (br, 2H), 1.70 (br, 8H), 1.52 (br, 8H), 1.16 (br, 6H), 1.07 (br, 6H). GPC: $\bar{M}_w = 92.0$ kDa, $\bar{M}_n = 26.9$ kDa, PDI = 3.4. TGA: $T_d = 320$ °C.

2.2. Instruments

¹H NMR spectra were recorded on a Varian NMR 400 MHz spectrometer using deuterated chloroform purchased from Cambridge Isotope Laboratories, Inc. The molecular weights of the polymers were determined by gel permeation chromatography (GPC, Tosoh GPC HLC-8320GPC ecocex) using polystyrene as the standard and THF as the eluent. Thermal gravimetric analysis (TGA) was conducted on a Mettler TGA50 thermal analysis system under a heating rate of 10 °C·min⁻¹. Absorption spectra of film



Scheme 1. Synthetic procedure for PBDT-3MT (i: Pd(PPh₃)₄, toluene/DMF (9:1, v/v), 110 °C, 60 h.) and structure of published two alkyl thiophene-3-carboxylate-based polymers, P3CTV and PCTBDT.

samples and of *o*-dichlorobenzene (*o*-DCB) solutions (concentration 1×10^{-6} mol·L⁻¹) were obtained using a Shimadzu UV-3101 PC spectrophotometer in the wavelength range 300–800 nm. The redox property of the synthesized copolymer was examined by cyclic voltammetry (model: EA161 eDAQ). The electrolyte solution employed was 0.10 M tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) in freshly dried acetonitrile. The Ag/AgCl and Pt wire (0.5 mm in diameter) electrodes were utilized as reference and counter electrodes, respectively. The scan rate was at 50 mV·s⁻¹.

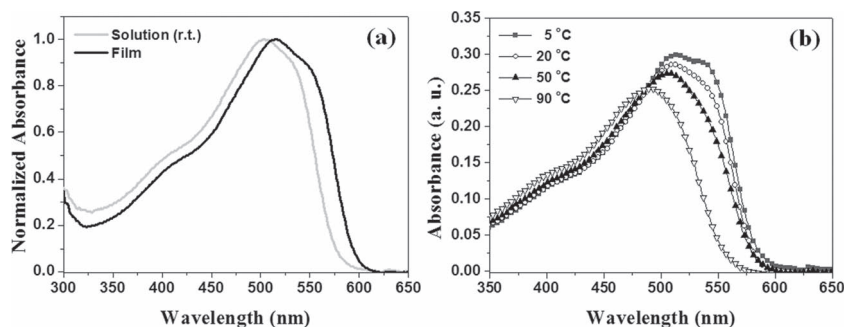


Figure 1. (a) UV-vis absorption spectra of PBBDT-3MT in *o*-DCB solution and film state. (b) UV-vis absorption spectra of PBBDT-3MT in *o*-DCB solution at various temperatures.

2.3. Fabrication and Characterization of PSCs

All devices reported here were fabricated on indium tin oxide (ITO) coated glass substrates. A 30 nm layer of PEDOT:PSS was spin coated on top of ITO and baked at 120 °C for 10 min. Subsequent device processing was performed in a glove box under a nitrogen atmosphere. A blend film of the copolymer and PC₇₁BM was spin coated on top of the PEDOT:PSS layer using a *o*-DCB solution and was dried at 90 °C for 10 min. Finally, a ~100 nm thick lithium fluoride (LiF)/aluminum (Al) electrode was deposited by a thermal evaporator (vacuum at 10^{-6} – 10^{-7} Torr) to produce a 0.0425 cm² active area using a mask. The *I*–*V* characteristics were measured with a computerized Keithley 2400 source meter in the dark and under AM 1.5G illumination at 100 mW·cm⁻² supplied by a solar simulator (Oriel, 1000 W). The spectral response was measured using a tungsten-halogen light source combined with a monochromator (Spectra Pro 2300, Acton Research). The monochromatic light from the monochromator was filtered for the UV, visible and IR range to remove harmonics and was modulated using an optical chopper at 350 Hz. The resulting photocurrent on the photovoltaic cell was measured using a lock-in amplifier (SR-830, Stanford Research). The power of the monochromatic light was measured using a calibrated optical power meter and a photodetector (Coherent Fieldmax II with UV to IR sensor heads and a Thorlabs PM100). All equipment and data acquisition were controlled by LabView.

3. Results and Discussion

The new copolymer, PBBDT-3MT was synthesized by the Stille coupling reaction of methyl-2,5-dibromo-thiophene-3-carboxylate (3MT) with a 2,6-bis(trimethyltin)-4,8-bis(2-ethylhexyloxy)benzo[1,2-*b*:4,5-*b'*]dithiophene in toluene/DMF in the presence of Pd(PPh₃)₄ as a catalyst (Scheme 1). The ¹H NMR spectrum of PBBDT-3MT (see Figure S1 in the Supporting Information) exhibited the chemical shift of thienyl-H next to the ester unit at 7.98 ppm and two thienyl-H of BDT at 7.4–7.7 ppm, which suggested that PBBDT-3MT is a regiorandom copolymer, because the multiproton peaks of the copolymer are similar to those of the published regiorandom copolymer (PCTBDT).^[29] The PBBDT-3MT showed good solubility in common organic solvents such as chloroform, THF, toluene and *o*-DCB. The number

averaged molecular weight was 92 kDa, and the polydispersity index (PDI) was 3.4 for PBBDT-3MT. The thermal stability of PBBDT-3MT was characterized by thermogravimetric analysis (TGA) in N₂. As shown in Figure S2 in the Supporting Information, PBBDT-3MT is thermally stable with a 5% weight-loss at temperatures above 320 °C. Figure 1 shows the absorption spectra of PBBDT-3MT in *o*-DCB solution and in thin films. The absorption maximum (λ_{max}) of 516 nm in the film state was slightly red-shifted by about 13 nm from that in *o*-DCB solution (503 nm). In particular, PBBDT-3MT showed strongly thermochromic behavior in the *o*-DCB at various temperatures, as shown in Figure 1(b). At temperatures exceeding 90 °C, PBBDT-3MT shows a single absorption band at λ_{max} of 488 nm. However, by decreasing the temperature, the absorption spectra of PBBDT-3MT were significantly red-shifted and the spectral shape at room temperature is considerably similar to that of the film state. This observed absorption behavior of PBBDT-3MT indicates that the copolymer has a very strong inter- and intra-chain interaction between polymers, even in solution states.^[25] Also, this result means that the methyl carboxylate group in the side chain did not produce much steric hindrance, compared to PCTBDT. The cyclic voltammetry (CV) studies were carried out on polymer thin film coated on a platinum plate electrode. As shown in Figure 2(a), the HOMO of PBBDT-3MT was estimated to be at –5.43 eV on the basis of the onset of oxidation (1.05 V). In order to determine the LUMO level (–3.36 eV), we combined the HOMO value in CV with the optical energy bandgap (2.07 eV) resulting from the absorption edge in its absorption spectrum. Compared to the HOMO of P3HT (–5.0 eV), PBBDT-3MT exhibited a much deeper HOMO level by 0.4 eV. The HOMO energy was also slightly lower than those of P3HTV (–5.26 eV) and PCTBDT (–5.36 eV).

The photovoltaic properties of BHJ made of the PBBDT-3MT copolymer and PC₇₁BM were investigated in a conventional device configuration of ITO (indium tin oxide)/poly(3,4-ethylene dioxythiophene):poly(styrene sulfonate) (PEDOT:PSS; 30 nm)/polymer: PC₇₁BM/LiF(1 nm)/

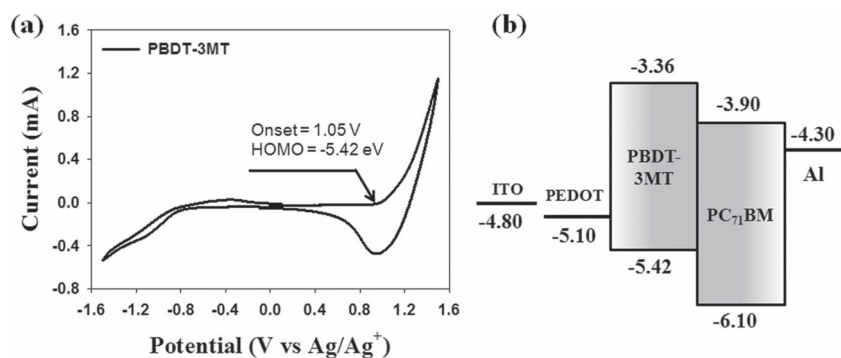


Figure 2. (a) Cyclic voltammogram of PBDT-3MT film on platinum plate electrode in the acetonitrile solution containing 0.1 M Bu₄NPF₆ at a scan rate of 50 mV·s⁻¹. (b) Energy level diagrams for PBDT-3MT and PC₇₁BM.

Al(100 nm) with a device area of 0.0425 cm². The active materials, PBDT-3MT and PC₇₁BM, were dissolved in an *o*-DCB and then the solution mixture was stirred at 50 °C for 12 h. After filtering the solution with acrodisc filter (0.45 μm), the photoactive layer was deposited by spin-coating on the ITO/PEDOT:PSS substrate. All PSC devices fabricated herein were thermally annealed in a N₂ atmosphere at 90 °C for 10 min before the deposition of the electrode. In order to obtain the best PSC performance, the active layer thickness and the blending ratio between copolymer and PC₇₁BM were systematically investigated as well. The results of the device performance are summarized in Table 1. Figure 3 shows the current density-voltage (*J*-*V*) characteristics under AM 1.5G solar irradiation (100 mW·cm⁻²) and the *J*-*V* curve of PSCs for the PBDT-3MT:PC₇₁BM weight ratios (1:1, 1:2, 1:3, and 1:4). Among the devices, the best performance was obtained at the weight ratio of 1:1, with *V*_{OC} = 0.84 V, *J*_{SC} = 10.50 mA·cm⁻², and an overall PCE of 3.53%. We also tested PBDT-3MT/PC₇₁BM (1:1 wt%)-based devices with different thicknesses of photoactive layer. A PSC device with an active

layer of 70 nm reached the PCE of 4.52%, with *J*_{SC} = 10.5 mA·cm⁻², *V*_{OC} = 0.86 V, and fill factor (*FF*) = 50%, as shown in Table 1. The high *V*_{OC} value corresponds to the low-lying HOMO level (-5.43 eV) obtained from electrochemical analysis.

Particularly, this high PCE of the PBDT-3MT-based PSC device was obtained without additional treatments, such as thermal/solvent annealing or introducing additives. To better understand the origin of the photovoltaic performance, atomic force microscopy (AFM) images were collected. As shown in Figure S2 in the Supporting Information, the AFM surface image of the

as-cast PBDT-3MT:PC₇₁BM (1:1) blend film showed good film-forming ability and miscibility. It indicates that the well-dispersed domain could increase the interfacial area for exciton dissociation and effective percolation for charge transport in the blend film, thus increasing the *J*_{SC} of the PBDT-3MT:PC₇₁BM device. Moreover, the highly optimized PCE value of 4.52% is around two times higher than that for reported P3HTV and PCTBDT. Although *FF* of the PBDT-3MT-based device increased from 37% to 50% by decreasing the thickness of the active layer, the value is relatively lower than that of a P3HT-based device (>60%). The modulation of the *FF* value is known to be influenced by a number of factors, such as the thickness, thermal treatments, film morphology and charge carrier mobility of the active layer.^[32–34] One of the important factors to be concerned with is the carrier mobility of the polymer in the OPV device. The mobility is well known to depend on the degree of regioregularity of the conjugated thiophene-based polymer. The PBDT-3MT is a regiorandom copolymer which is not good for forming well-defined polycrystalline film.^[25] As shown in Figure S3 in the Supporting

Table 1. Device performance of photovoltaic cells based on new copolymer and published polymers, P3CTV and PCTBDT.

Polymer	Polymer:PC ₇₁ BM [wt%]	Thickness [nm]	<i>J</i> _{SC} [mA·cm ⁻²]	<i>V</i> _{OC} [V]	<i>FF</i> [%]	PCE [%]
PBDT-3MT	1:1	77	10.50	0.84	40	3.53
	1:2	78	8.25	0.86	47	3.33
	1:3	76	4.63	0.84	43	1.67
	1:4	77	4.06	0.85	46	1.59
	1:1	70	10.50	0.86	50	4.52
	1:1	78	10.58	0.84	44	3.91
	1:1	85	5.47	0.85	37	2.60
P3CTV	1:2 (PC ₆₁ BM)	80	5.47	0.86	43	2.01 ^[26]
PCTBDT	1:1 (PC ₆₁ BM)	135	6.94	0.80	42	2.32 ^[29]

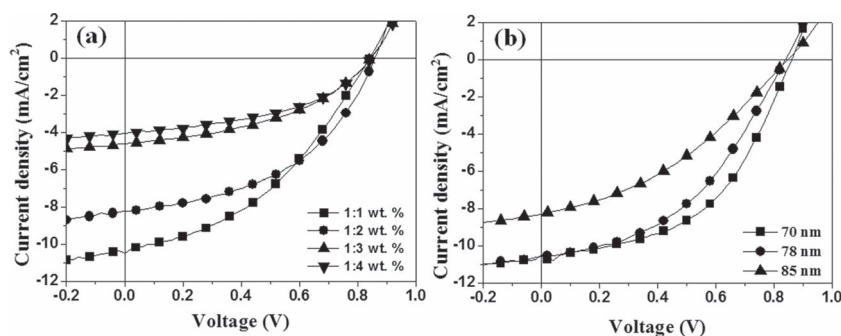


Figure 3. (a) Current density-voltage (J - V) characteristics of PV devices based on PBDT-3MT:PC₇₁BM polymer blends with different weight ratios. (b) PBDT-3MT:PC₇₁BM (1:1 wt %) polymer blends with different concentrations fabricated from *o*-DCB solutions.

Information, the thin film transistor (TFT) device based-on PBDT-3MT showed a low hole mobility of $4.18 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, which is much lower than that of regioregular poly(3-hexylthiophene) (P3HT). This could be one of the reasons for the lowering FF value of the regiorandom PBDT-3MT-based PV device. As shown in Figure 4, the shape of the external quantum efficiency (EQE) of the PBDT-3MT:PC₇₁BM (1:1 wt %) device was very similar to its absorption spectrum. This indicates that all absorption in the polymer contributed to the photovoltaic conversion. The maximum EQE value of the device based on PBDT-3MT was reached at 550 nm.

4. Conclusion

A new alternating copolymer, PBDT-3MT, was synthesized by the Stille coupling reaction of methyl-2,5-dibromothiophene-3-carboxylate with a 2,6-bis(trimethyltin)-4,8-bis(2-ethylhexyloxy)benzo[1,2-*b*:4,5-*b'*]dithiophene. The introduction of the methyl carboxylate group into the thiophene ring provides the copolymer with a lower

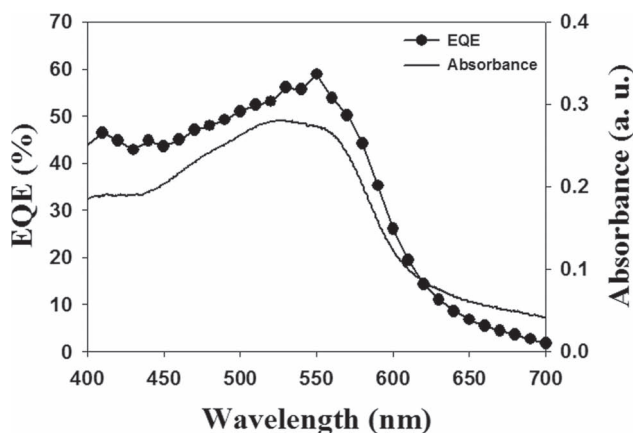


Figure 4. External quantum efficiency and solid film absorption spectra of PBDT-3MT:PC₇₁BM (1:1 wt %).

HOMO level. Although PBDT-3MT is a regiorandom copolymer, the optical property of the copolymer showed a very strong inter- and intra-chain interaction between polymers in the solution state. The photovoltaic device based-on a PBDT-3MT:PCBM bulk heterojunction exhibited a high PCE of 4.52%, with $J_{SC} = 10.5 \text{ mA cm}^{-2}$, $V_{OC} = 0.86 \text{ V}$ and $FF = 50\%$. These results indicate that 3MT unit is a promising candidate for an effective acceptor for the design of D-A type photovoltaic polymers.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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