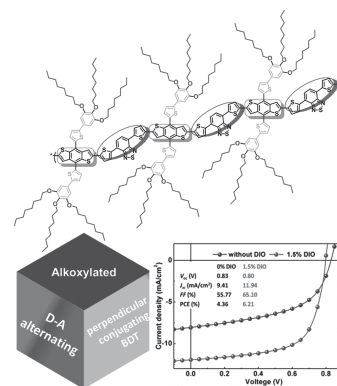


Novel Donor–Acceptor Polymer Containing 4,7-Bis(thiophen-2-yl)benzo[c][1,2,5]thiadiazole for Polymer Solar Cells with Power Conversion Efficiency of 6.21%

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In order to improve the solution processability of 4,7-bis(thiophen-2-yl)benzo[c][1,2,5]thiadiazole (DTBT)-based polymers, novel donor–acceptor polymer **PTOBDTDTBT** containing DTBT and benzo[1,2-b:4,5-b']dithiophene (BDT) with conjugated side chain is designed and synthesized with narrow band gap 1.67 eV and low lying HOMO energy level -5.4 eV. The blend film of **PTOBDTDTBT** and PC₇₁BM exhibits uniform and smooth film with root-mean-square (RMS) surface roughness 1.15 nm because of the excellent solubility of **PTOBDTDTBT** when six octyloxy side chains are introduced. The hole mobility of the blend film is measured to be $4.4 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ by the space-charge-limited current (SCLC) model. The optimized polymer solar cells (PSCs) based on **PTOBDTDTBT**/PC₇₁BM exhibits an improved PCE of 6.21% with $V_{oc} = 0.80$ V, $J_{sc} = 11.94 \text{ mA cm}^{-2}$ and FF = 65.10%, one of the highest PCE in DTBT containing polymers.



1. Introduction

Bulk heterojunction polymer solar cells (PSCs) have attracted much attention for their unparalleled solution processability and high efficiency, which show potential application in flexible large area devices.^[1] By means of the materials design and device optimization, power conversion efficiencies (PCEs) surpassing 8% have been realized for PSCs.^[2] The most efficient conjugated polymers reported were designed as donor–acceptor (D–A)

alternating structures, for instance, the copolymers of benzo[1,2-b:4,5-b']dithiophene (BDT)^[2] derivatives and matched acceptors like thieno[3,4-c]pyrrole-4,6-dione (TPD),^[3] diketopyrrolopyrrole (DPP),^[4] and side-group electron-withdrawing thieno[3,4-b]-thiophene (TT).^[5] The above-mentioned D–A polymers possess superior bandgap (E_g) and good solubility in which the alkyl chain can be introduced to both the donor and acceptor units. However, the D–A polymers based on TT or TPD can hardly match any other donor units except BDT, which will be difficult to improve the PCE through materials design.

4,7-Bis(thiophen-2-yl)benzo[c][1,2,5]thiadiazole (DTBT) was one of the most popular monomers with high planarity and regularity for designing narrow E_g D–A polymers in PSCs application. Unlike TT or TPD, DTBT itself was a D–A–D-type dye containing strong electron-donating thiophene group and electron-withdrawing benzo[c][1,2,5]thiadiazole group, which was easy to build narrow E_g polymers when copolymerized with any

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π bridges, such as alkylated fluorene,^[6] anthracene,^[7] carbazole,^[8] silafluorene,^[9] indacenodithiophene,^[10] BDT,^[11] and so on with PCE from 2.4% to 6.17%. Despite these advantages, the poor solubility of DTBT caused by the strong π - π stacking requires the π bridge highly alkylated. PCDTBT was firstly reported by Leclerc and co-workers^[8a] with PCE of 3.6%; and its PCE can be further optimized higher than 6.0% by inserting titanium oxide or PFN as the charge transporting layer.^[8b-d] Although branched alkyl chain was introduced to improve the solubility, however, PCDTBT was not completely soluble in chloroform when the weight-average molecular weight (M_w) higher than 60 kDa.^[12] PBDTTBT^[11a] employing thiophene-substituted BDT as the π bridge can improve the PCE to 5.66%, which was ascribed to the enhanced hole mobility and planarity, however, the yield of PBDTTBT was only 34%, lower than general polymerization. We inferred the solubility of PBDTTBT was not good enough for completely soluble in common organic solvents. Polymer containing DTBT with ideal solubility was reported by Li and co-workers.^[10] Tetradodecyl substituted indacenodithiophene can provide high solubility for PIDT-DTBT, which exhibited smooth film when blended with [6,6]-phenyl C_{71} butyric acid methyl-ester (PC₇₁BM) with root-mean-square (RMS) surface roughness 0.91 nm, and high PCE of 6.17% was obtained after device modification. The only fly in the ointment was that the indacenodithiophene monomer cannot be purified completely, which result in relative low molecular weight of PIDT-DTBT.

According to the work reported by Stefan and co-workers^[13] alkyl substituted bithienyl can improve the solubility of the corresponding polymers, which resulted in higher molecular weight. In addition, Wang et al.^[14] have also discussed that the side chain can obviously influence the molecular weight and photovoltaic performance of the polymers. We propose that the PCE of DTBT-based

copolymers can be further improved by designing high solubility donor unit to enhance their solution processability and molecular weight without changing their photophysical and electrochemical characteristics seriously. The aryl-substituted BDT containing polymers have exhibited excellent photovoltaic performance for their high planarity and hole mobility.^[15] So, in this communication, high solubility 4,8-bis(2-(3,4,5-tris(octyloxy)phenyl)thiophene-2-yl)benzo[1,2-b:4,5-b']dithiophene (TOBDT) with six alkoxyated substituents was designed to improve the processability of the polymer (Scheme S1, Supporting Information).

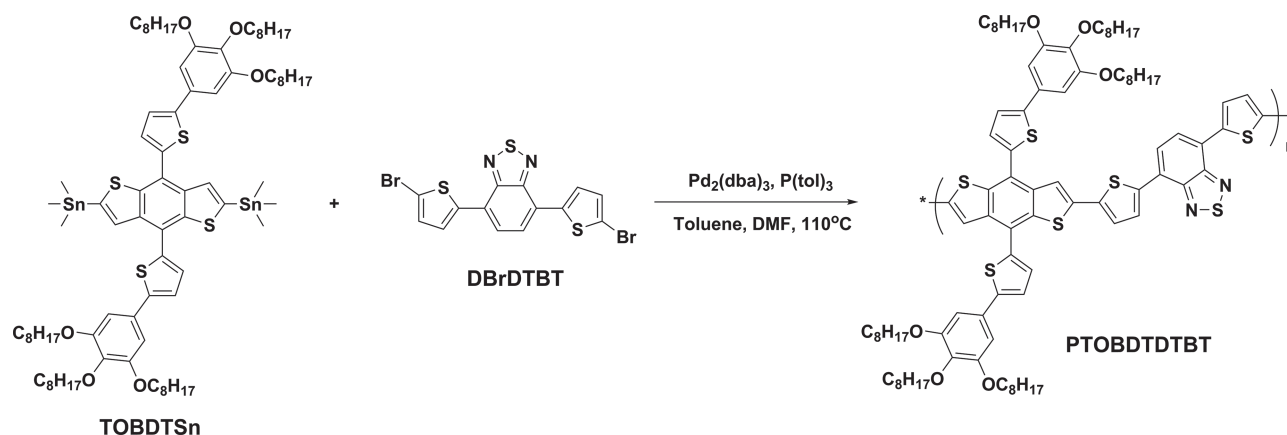
2. Experimental Section

The synthesis and characterization of all the compounds were described in the Supporting Information. Device fabrication and characterization were also described in the Supporting Information.

3. Results and Discussion

3.1. Synthesis and Characterization of PTOBDTDTBT

Polymer **PTOBDTDTBT** based on TOBDT and DTBT was synthesized by Stille coupling reaction as shown in Scheme 1. Both the monomers TOBDTSn and DBrDTBT can be purified by recrystallization from isopropanol and dimethylformamide, respectively, which is conducive to improve the molecular weight. **PTOBDTDTBT** was purified through Soxhlet extraction and silica gel column chromatography with $CHCl_3$ as the eluent in high yield 91.6%, indicating high solubility of the polymer in $CHCl_3$, in addition, **PTOBDTDTBT** can be easily dissolved in tetrahydrofuran (THF), chlorobenzene, *o*-dichlorobenzene (*o*-DCB), and so



■ Scheme 1. Synthesis of polymer PTOBDTDTBT.

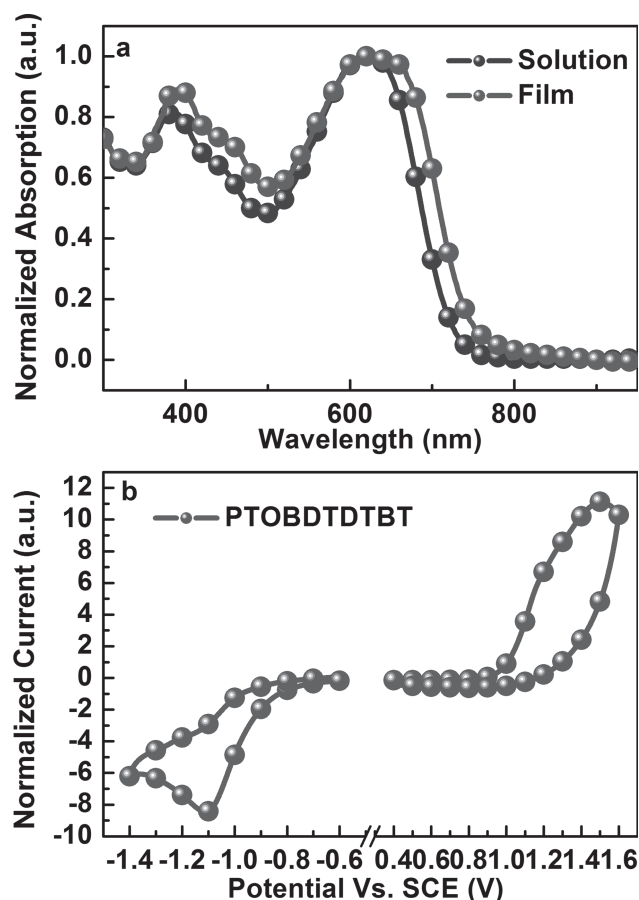


Figure 1. UV-vis absorption and electrochemical properties of **PTOBDDTBT**. a) Absorption spectra in CHCl_3 solution and in film state. b) Cyclic voltammogram of as casted film vs the SCE in acetonitrile solution.

on. The gel permeation chromatography (GPC) measurement with mono-disperse polystyrene as standard and THF as the eluent showed that **PTOBDDTBT** has high number-average molecular weight (\bar{M}_n) of 72 KDa with a polydispersity index (PDI) of 2.15. The decomposition temperatures (T_d) of **PTOBDDTBT** was located at 370 °C (Figure S1, Supporting Information), indicating sufficient thermal stability for PSCs applications. Due to the six octyloxy side chains and extended conjugating structure of TOBDT, **PTOBDDTBT** exhibited excellent film-forming ability (Figure S2, Supporting Information) and high hole mobility $4.4 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (Figure S4, Supporting Information) with wide absorption spectra (300–780 nm). The optimized PSC device based on **PTOBDDTBT**/PC₇₁BM exhibited an improved PCE of 6.21% with $V_{oc} = 0.80 \text{ V}$, $J_{sc} = 11.94 \text{ mA cm}^{-2}$, and FF = 65.10%.

3.2. Photophysical Property

The UV-vis spectra of **PTOBDDTBT** in CHCl_3 and in film state were shown in Figure 1a. In CHCl_3 solution,

PTOBDDTBT showed an absorption maximum at 622 nm with two weaker peaks at 386 and 447 nm, respectively. In film state, the spectrum becomes broader with a new shoulder peak at 662 nm, which was a common phenomenon for the conjugated polymers, owing to the aggregation of the polymer main chains in the solid films. Interestingly, the absorption of **PTOBDDTBT** in the range of 300–500 nm was stronger and broader than previously reported results,^[6–10,11a] the reason was probably that TOBDT showed extended conjugation length in the vertical direction and the absorption around high energy originates from the π – π^* transition of the polymer main chain and side chain, which may be favorable to absorb more light. Noticing the absorption peaks before 500 nm were red-shifted to 393 and 453 nm in film state compared to those in CHCl_3 solution as well the spectra became broader, indicating that the strong interchain aggregation occurred when tris(octyloxy)phenyl was introduced. The aggregation was obvious as shown in Figure S5 (Supporting Information), the maximum absorption was blue-shifted to 602 nm when the solution was heated to 90 °C. From the onset absorption 744 nm (λ_{onset}) in the thin film, one could estimate the optical E_g of **PTOBDDTBT** was 1.67 eV, lower than previously reported results.^[6–10,11a] The narrower E_g can be mainly attributed to a more ordered and planar structure in the main chain of **PTOBDDTBT**.

3.3. Electrochemical Property

As shown in Figure 1b, the cyclic voltammogram of **PTOBDDTBT** presented one oxidation process ($E_{onset}^{ox} = 1.00 \text{ V}$ versus the standard calomel electrode (SCE)) and one reduction process ($E_{onset}^{red} = -0.86 \text{ V}$ vs SCE). A deep-lying HOMO energy level of -5.40 eV was estimated, which was at the ideal range to ensure better air stability and greater attainable V_{oc} in the device.^[16] The LUMO energy level was determined to be -3.73 eV according to the HOMO and optical E_g , which fitted reasonably well with the required electronic levels (E_{LUMO} level between 3.7–4.0 eV) for PSCs utilizing PC₇₁BM as the acceptor.^[17]

3.4. Photovoltaic Property

Photovoltaic properties of **PTOBDDTBT** were investigated in devices with the traditional structure of ITO/PEDOT:PSS/**PTOBDDTBT**:PC₇₁BM/Ca/Al. PSCs were fabricated from *o*-DCB solutions with varied stoichiometry, concentrations of 1,8-diiodooctane (DIO) and spin-coating speeds (Figure S6–S7, Supporting Information). PC₇₁BM was selected because of its complementary absorption in the visible region. As expected, the blend **PTOBDDTBT**:PC₇₁BM active layer exhibited uniform and smooth film with RMS surface roughness 1.15 nm because of the excellent

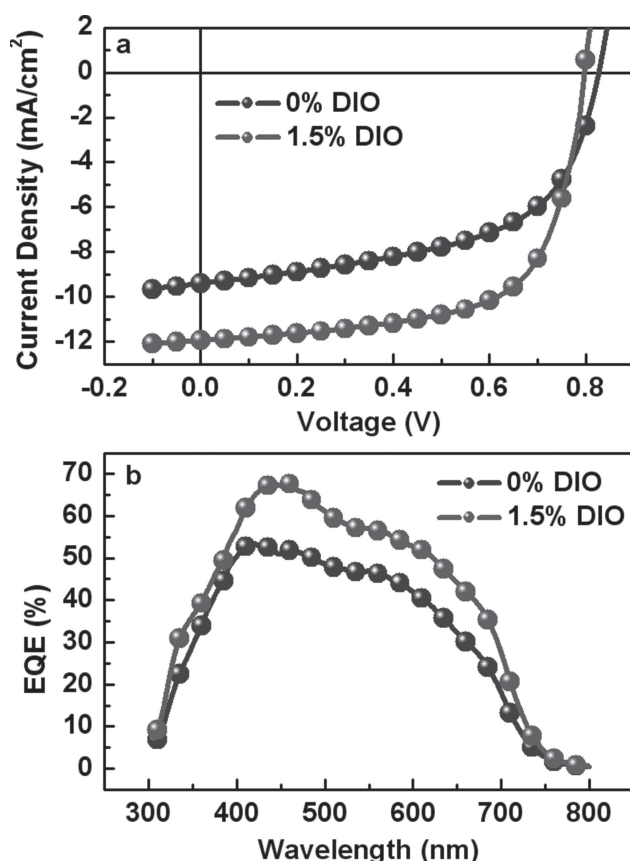


Figure 2. The J - V curves and EQE spectra of **PTOBDDTBT**:**PC₇₁BM** devices. a) J - V curves under illumination of AM 1.5G, 100 mW cm⁻², with and without DIO. b) EQE spectra, with and without DIO.

solubility of **PTOBDDTBT** in *o*-DCB solution (Figure S2a, Supporting Information). The devices were measured under the illumination of AM 1.5G (100 mW cm⁻²). The optimized **PTOBDDTBT**:**PC₇₁BM** ratio was 1:2 (w/w) for device without additive, and it showed a V_{oc} = 0.83 V, J_{sc} = 9.41 mA cm⁻², FF = 55.77% and PCE = 4.36%. The low J_{sc} and FF were because of the poor phase separation in the active layer according to the atomic force microscopy (AFM) together with the transmission electron microscopy (TEM) images (Figure S2b, Figure S3a, Supporting Information). When 1.5% (w/w) DIO was added, nanoscale phase separation was observed (Figure S2d, Figure S3b, Supporting Information), which enabled a large interface area for exciton dissociation and a continuous percolating path for hole and electron transport to the

Table 1. PSCs characteristics of devices with and without DIO.

PTOBDDTBT / PC₇₁BM ratio	Thickness [nm]	V_{oc} [V]	J_{sc} [mA cm⁻²]	FF [%]	PCE_{max}/PCE_{ave}^{c)} [%]
1:2 ^{a)}	95	0.83	9.41	55.77	4.36 (4.28)
1:2 ^{b)}	96	0.80	11.94	65.10	6.21 (6.13)

^{a)} 0% DIO, ^{b)} 1.5% DIO, ^{c)} The average PCE was obtained from over eight devices.

corresponding electrodes, as a result, the J_{sc} and FF were improved to 11.94 mA cm⁻² and 65.10%, respectively, and higher PCE of 6.21% was obtained as shown in Figure 2a. The optimized PSCs characteristics of the devices with and without DIO were summarized in Table 1. More interestingly, the V_{oc} of 0.80 V was well matched with the result calculated from the empirical formula:^[17a] $V_{oc} = (1/e)(|E_{HOMO}^{Donor}| - |E_{LUMO}^{PCBM}|) - 0.3$ V, where e is the elementary charge and using -4.3 eV for the LUMO energy of **PC₇₁BM**. However, the V_{oc} was slightly lower than other BDT and DTBT containing polymers,^[11] the reason may be the strong electron-donating property of octyloxy side chain especially when the phenyl was *p*-substituted. Both the devices show efficient incident photo conversion efficiency between 400 and 700 nm, especially when DIO was added, the external quantum efficiency (EQE) value of 67.6% was obtained as shown in Figure 2b. The J_{sc} (11.34 mA cm⁻²) calculated from the integration of the EQE spectra agrees well with the J_{sc} (11.94 mA cm⁻²) recorded from the J - V measurements.

4. Conclusions

In order to improve the solubility of polymers based on DTBT, we have successfully designed and synthesized a D-A polymer **PTOBDDTBT** with six long alkoxy side chains, which exhibited appropriate photophysical, electrochemical characteristics, and molecular weight. Together with its good thermal stability and film-forming ability, **PTOBDDTBT** exhibited excellent photovoltaic performance when employing **PC₇₁BM** as the acceptor with PCE of 6.21%, V_{oc} = 0.80 V, J_{sc} = 11.94 mA cm⁻², and FF = 65.10%. This is one of the most efficient PSCs based on DTBT containing polymers. Solubility of conjugated polymers can seriously influence the molecular weight and photovoltaic effect. In this communication, it firstly shows that phenyl trialkoxy group is an excellent substituent to provide good solubility on designing narrow E_g polymers, meanwhile, retains the parent polymer's high photovoltaic performance. Further optimization of both the molecule and device structures on this system is underway in our group for better photovoltaic properties.

Supporting Information

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

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