

Highly Efficient 2D-Conjugated Benzodithiophene-Based Photovoltaic Polymer with Linear Alkylthio Side Chain

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Supporting Information

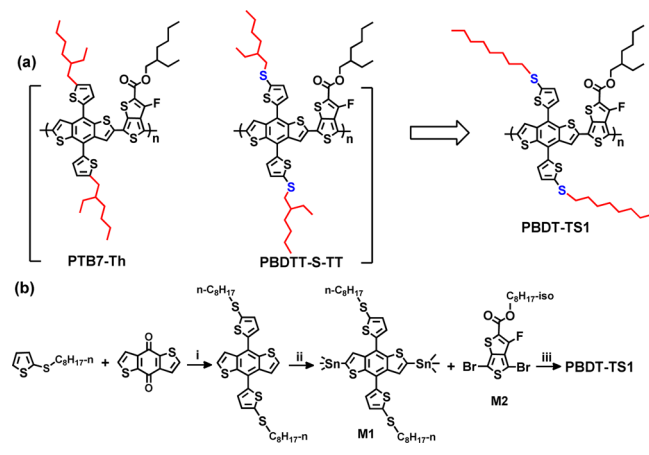
Recently, polymer solar cells (PSCs) have been the subject of extensive study because of their potential applicability in lightweight, flexible, colorful and/or transparent large-area devices.^{1,2} To improve photovoltaic performance of PSCs, tremendous efforts have been devoted to designing, synthesizing and optimizing photovoltaic polymers with superior photovoltaic properties, such as suitable molecular energy levels, broad absorption band, high hole mobility, and so on.^{3–12} Since the first introduction of 2-alkylthienyl as the conjugated side groups in the benzo[1,2-*b*:4,5-*b'*]dithiophene (BDT) units,¹³ the alkylthienyl substituted BDT (BDT-T) units have been widely used to construct novel photovoltaic polymers^{14–20} and thereby the power conversion efficiencies (PCEs) have been boosted to several new heights in the field of PSCs.^{20–23} For instance, Chen et al.²³ lately reported a photovoltaic polymer (named as PTB7-Th, see Scheme 1a) with superior photovoltaic properties by incorporating the 2-(2-ethylhexyl)-thienyl group into the BDT unit of the well-known photovoltaic polymer, PTB7.

Alternatively, others have successfully incorporated sulfur atom in BDT unit and synthesized efficient photovoltaic polymers based on alkylthio-substituted BDT with V_{oc} exceeding 0.9 V.^{24,25} Likewise, branched alkylthio was also introduced in BDT-T-based polymer and an improved V_{oc} of 0.84 V was obtained in the PSCs based on PBDTT-S-TT (see Scheme 1a).¹⁹ As listed in Table 1, the J_{sc} of these BDT-T-based polymers (PTB7-Th, PBDTT-S-TT) still kept at a relatively low level, which was the limiting factor for further improvement of PCE. That is to say, to simultaneously achieve high V_{oc} and J_{sc} is still a great challenge for molecular design of novel photovoltaic polymers until now.

Alkyl chains are fundamental units in designing organic or polymeric semiconductors for a well balance of close intermolecular packing, high crystallinity, and excellent device performance.^{26–30} As reported, the size and topology (e.g., linear, branch) of the alkyl chains appended to the polymer backbone was an critical factor impacting the photovoltaic parameters of the corresponding PSCs.^{30–34} Considering that the branched alkyls have positive influence in keeping good solubility but adverse effect on the structural order and thereby charge transport properties, the nonconjugated side groups in photovoltaic polymers must be carefully selected. Several studies previously demonstrated that the octyl-based polymers can deliver a slightly reduced V_{oc} but with a significantly improved J_{sc} relative to the 2-ethylhexyl-based polymers.^{31,32} As a result, we try to improve the J_{sc} of the BDT-T and thieno[3,4-*b*]thiophene (TT) copolymers (PBDTTT-based polymer) by introducing linear alkylthio chains in BDT-T unit without sacrificing the high V_{oc} of the original backbone.

In the current work, to integrate the modulating effects of the two-dimensional structure on reaching higher mobility, the alkylthio groups on realizing lower HOMO level and the straight alkyls on achieving ordered intermolecular stacking, we designed a novel PBDTTT-based polymer (namely PBDT-TS1, see Scheme 1a) by replacing 2-ethylhexyl with octyl, which could be seen as an optimized structure of the two reported polymers, i.e. PBT7-Th²³ and PBDTT-S-TT.¹⁹ The synthesis route of PBDT-TS1 was described in Scheme 1b. The monomer M1 was prepared by identical procedures, as previously reported.^{13,19} The polycondensation was carried out through Stille coupling reaction using Pd(PPh₃)₄ as catalyst

Scheme 1. (a) Molecular Structure of Two Reference Polymers and Target Polymer; (b) Synthesis Procedure of PBDT-TS1



Generally, higher short-circuit current densities (J_{sc}) and improved PCEs have been achieved in the PSCs based on the BDT-T-based conjugated polymers, whereas the open-circuit voltages (V_{oc}) are still limited. Recently, our group developed a novel strategy to promote the V_{oc} of BDT-T-based polymers by incorporating the fluorine atom in the BDT-T units.¹⁸

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Table 1. Photovoltaic Results of the Highly Efficient PBDT-TT-Based Photovoltaic Polymers

polymers	V_{oc} (V)	J_{sc} (mA/cm ²)	FF (%)	PCE (%)	ref
PTB7-Th	0.77	14.99	63.92	7.42	19
PBDT-TT-S-TT	0.84	15.32	65.49	8.42	19
PBDT-TS1 ^a	0.80 (0.80 ± 0.01)	17.46 (17.37 ± 0.38)	67.9 (66.1 ± 0.13)	9.48 (9.19 ± 0.18)	this work

^aThe average values and variances of 100 devices are provided in parentheses, see the Supporting Information for details.

in good yields. Gel permeation chromatography (GPC) analysis showed the molecular weight (M_n) of PBDT-TS1 is 29.4 K with a moderate polydispersity index (PDI) of 2.21. As illustrated in the TGA plot (Figure 1a), PBDT-TS1 exhibits a decomposition temperature (T_d) at ca. 360 °C.

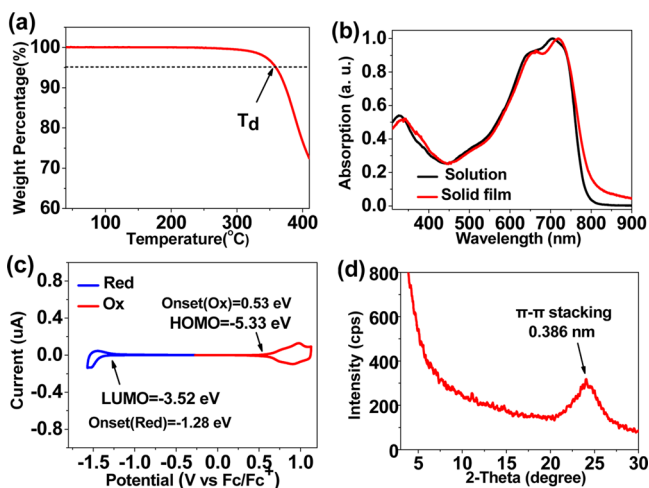


Figure 1. Basic characterizations of the polymer PBDT-TS1: (a) TGA plot; (b) normalized UV-vis absorption spectra in solution and solid film; (c) cyclic voltammogram; (d) XRD pattern.

Absorption spectra of PBDT-TS1 in solution and in solid state are shown in Figure 1b. PBDT-TS1 possesses two absorption peaks centered at 655 and 705 nm. The film absorption onset of 820 nm corresponds to a low optical bandgap of 1.51 eV, which is lower than that of PTB7-Th (1.58 eV) and PBDT-TT-S-TT (1.57 eV).¹⁹ The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels of PBDT-TS1 are respectively determined to be -5.33 eV and -3.52 eV by electrochemical cyclic voltammetry (see Figure 1c). Interestingly, as indicated by the X-ray diffraction (XRD) pattern in Figure 1d, no clear peak could be found in lamellar packing, whereas the feature of π - π stacking ($d_{010} = 3.86$ Å) is pronounced in PBDT-TS1 film, which is seldom observed in PBDT-TT-based polymers. Obviously, the combination of good thermal stability, suitable HOMO level, broad absorption, and strong π - π stacking effect makes PBDT-TS1 a promising donor material for highly efficient PSCs.

Herein, the photovoltaic properties of PBDT-TS1 were evaluated by a simple conventional device structure³⁵ of ITO/PEDOT:PSS/Polymer:PC₇₁BM/Mg/Al. Then, 1,8-diiodooctane (DIO) was utilized to optimizing the morphology and the active layers were treated with methanol according to our previous work.³⁶ The device optimization details of PBDT-TS1 are enumerated in Table S1 and Figure S1 in the Supporting Information. Under the optimized conditions with the D/A weight ratio of 1:1.5 and DIO volume amount of 3%, the average PCE of 9.19% was obtained from 100 devices under the

illumination of AM 1.5G (100 mW/cm²) with a cell area of 4 mm². The device parameters and the standard deviation of 100 devices were all listed in Table 1 and Figure S2 in the Supporting Information. For the best-performing device, a PCE as high as 9.48% was achieved with a V_{oc} of 0.80 V, a J_{sc} of 17.46 mA/cm², and a fill factor (FF) of 67.9%, as depicted in Figure 2a. The J_{sc} calculated from the EQE curve in Figure 2b was

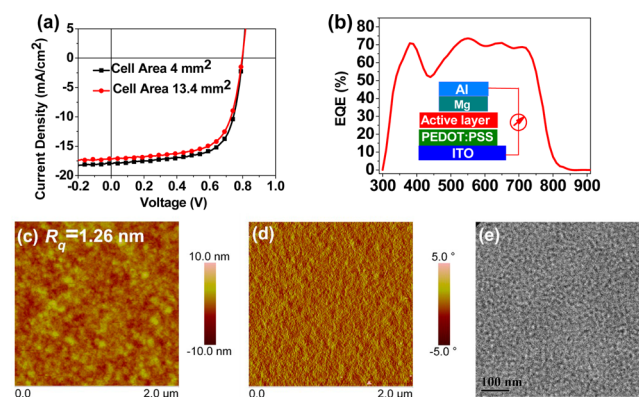


Figure 2. (a) J - V curves, (b) EQE curve, (c) AFM height image, (d) AFM phase image, and (e) TEM image of the best-performing PBDT-TS1:PC₇₁BM-based PSC with the simple conventional architecture.

quite consistent with the result from J - V test within 5% error. The PSC with a larger cell area (13.4 mm²) was also fabricated and a considerable PCE of 9.12% was still obtained in our laboratory, which was depicted in Figure 2a. This device was sent to National Institute of Metrology, China and certified with a slightly lower PCE of 8.60% (see Figure S3 in the Supporting Information). The dropped value should be ascribed to the degradation of conventional device architecture.⁵ This certification showed our results are reliable. Clearly, PBDT-TS1 is one of the outstanding photovoltaic polymers reported to date.

As observed in atomic force microscopy (AFM) and transmission electron microscopy (TEM) images (see Figure 2c-f), the low RMS roughness of 1.26 nm and formation of nanoscale phase separation with the appropriate feature size of ~20 nm in the optimized film of PBDT-TS1:PC₇₁BM are favorable for efficient charge separation and transport.^{1,3,11} In addition, XRD pattern and space-charge-limited current (SCLC) characterizations of the blend film were also performed (see Figure S4 in the Supporting Information). The ordering feature of π - π stacking was still apparent in the PBDT-TS1:PC₇₁BM-based blend film. A high hole mobility of 1×10^{-2} cm²/(Vs) was recorded for PBDT-TS1, which was approximately 1 order of magnitude higher than that of PTB7-Th or PBDT-TT-S-TT.¹⁹ Accordingly, these positive factors collectively contributed to the photocurrent enhancement as well as improved FF.

In conclusion, starting from two efficient photovoltaic polymers, a novel two-dimensional conjugated BDT-based

polymer, PBDT-TS1 was designed, synthesized by introducing linear side chain and a high PCE of 9.48% was achieved by PBDT-TS1:PC₇₁BM-based PSC evaluating with the simple conventional device. More importantly, due to the high starting point acquired in simple conventional device, PCEs of 10% or even higher would be realized in single-junction PSC by integrating more efficient device structures, such as inverted, plasmonic, or microcavity architectures.^{20–23,37}

■ ASSOCIATED CONTENT

● Supporting Information

Experimental details of the synthesis of PBDT-TS1, device fabrication details, and characterizations of the PSCs (i.e., measurements and instruments used). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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