Synthesis and Photovoltaic Properties of a Copolymer based on thieno [2, 3-f] benzo[1,2-b:4,5-b']dithiophene (BDT) and [3,4-c]pyrrole-4,6-dione (TPD) is one of the most researched donor materials. And the PCE based on BDT-TPD has achieved power conversion efficiencies (PCE) from 2% to 10.1% [2-3]. However, as the analogue of BDT, the copolymer based on thieno [2, 3-f] benzofuran(TBF) and thienopyrroledione(TPD) has never been reported. In theory, the polymers based TBF were expected to have a deeper HOMO energy, for the stronger electronegativity of the oxygen atom compared with that of the sulfur atom and that will be beneficial for obtaining high $V_{oc}[4]$. At the same time, the smaller radius of furan in comparison with thiophene could make the TBF bone more planar [5], which could facilitate charge transporting to improve the $J_{sc}$ and Fill factor (FF) of solar devices.

Herein, we designed and synthesized a novel donor-acceptor type conjugated polymer PTBFTPD based on two-dimensional (2D) conjugated alkylthienyl substituted thieno[2,3-f]benzofuran (TBF) and thienopyrroledione (TPD) unit, which was applied as donor material for bulk heterojunction solar cells. The novel polymer possessed a narrow bandgap of 1.83 eV, a deep HOMO energy level (-5.64 eV) and a closer π−π stacking. After conventional devices were fabricated using PTBFTPD as donor blending with PC70BM as acceptor, a power conversion efficiency (PCE) of 4.33% with a high open circuit voltage ($V_{oc}$) of 1.09 V was obtained. The result indicates the promising potential of thieno [2, 3-f] benzofuran unit for high efficient polymer solar cells with a high voltage.
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2. Experimental

2.1. Materials and general characterization method

All reagents were purchased from commercial sources without further purification. The monomer TBF-T was synthesized according to the literature [6], and the other monomer TPD was prepared by following literature procedure [7]. UV-Vis spectra was studied via a Beijing Purkinje General-TU-1901 spectrophotometer. The 1H-NMR spectra was collected on a Bruker AV 400 spectrometer operating at 400 MHz in deuterated chloroform solution. Cyclic voltammetry of polymer film was conducted in acetonitrile with 0.1 M of tetrabutylammonium hexafluorophosphate with a scan rate of 100 mV/s. GPC were performed on a Waters 410 differential refractometer.

2.2. Device fabrication and characterization

The PSCs were fabricated as follows: ITO-coated glass substrates (15 Ω/sq) were cleaned with detergent, deionized water, acetone and isopropyl alcohol. A thin layer (ca. 40 nm) of PEDOT:PSS(Baytron® P VPAI 4083, was first filtered via 0.45 um polytetrafluoroethylene (PTFE) filter and spin-coated on the pre-cleaned ITO-coated glass substrates at 3000 rpm and baked at 150 °C for 10 min under ambient conditions. The blend solution of polymer:PC70BM was dissolved in chlorobenzene (CB) with a weight ratio of 1:1.5 and filtered with a 0.2 mm PTFE filter. The blend solution was stirred for 10 h at ambient temperature and for 2 h at 80 °C. Then the active layer was spin-coated on PEDOT: PSS modified ITO coated glass and annealed on a hot plate at 100 °C for 30 min, which typically gave an active layer of 100-140 nm thickness according to different spinning speed. Following, a solution of 0.2 mg/mL PFN in methanol was spun coated onto the active layer, which was with a thickness about 5 nm. At the final stage, the substrates were pumped down to high vacuum (<3×10^-6 par), aluminum (100 nm) was thermally evaporated atop the active layer through shadow masks to define the active area of the devices. The active area of device defined by shadow mask was 0.1 cm^2. The current density–voltage (J–V) characteristics were recorded with a Keithley 2420 source measurement unit under simulated 100 mW/cm^2 (AM 1.5 G) irradiation from a Newport solar simulator. Light intensity was calibrated with a standard silicon solar cell.

![Synthetic route of polymer](image)

**Figure 1.** Synthetic route of polymer

2.3. Synthesis of PTBFTPD

As displayed in Figure 1, the synthesis route was as following: TBF-T (250 mg, 0.280 mmol) and TPD-Br (119 mg, 0.280 mmol) were charged into a 25 mL round bottom flask with a condenser under N2 protection. After degassed twice, dry toluene (10 mL), Pd2(dba)3P(o-tol)3 (5 mg) and P(o-tol)3 (10 mg) were added into the flask consequently. The resulting mixture was heated to 110 °C for 48 h. The reaction was end-capped with 2-bromothiophene and 2-tributylstannylthiophene. The mixture was poured into methanol and the precipitate was collected. Then the mixture was purified by Soxhlet extraction with
acetone, hexane and chloroform for 12h in order. The chloroform fraction was precipitated in methanol. Finally, the polymer was collected by filtration and dried under vacuum at 50 °C overnight to obtain a dark-red solid (140 mg, 60.3% yield). GPC (THF): M<sub>n</sub>=9.4 kDa; M<sub>w</sub>=18.1kDa; PDI =1.92. ^1H-NMR (400 MHz, CDCl<sub>3</sub>): d: 9.32-8.55 (br, 2H), 8.41–7.68 (br, 1H), 7.02-6.42 (br, 3H), 3.29–2.62 (br, 6H), 1.24-0.53 (br, 45H)

3. Discussion

![Figure 2](image)

Figure 2. a) the UV-Vis spectra of PTBFTPD in solution and film; b) the CV profile of PTBFTPD; c) XRD patterns of pristine PTBFTPD in film state; d) the PCE of PTBFTPD: PC70BM (1:1.5, w/w), using different ratio of DIO and annealed 100 °C for 30 min.

3.1. Optical properties

The UV-Vis absorption spectra of PTBFTTPD being measured in chloroform solution and thin film state were shown in Figure 2a. PTBFTTPD exhibited broad and intensive absorption in the range of 300-650 nm. Meanwhile, PTBFTTPD mainly possessed two absorption bands in both solution and in film state. And the high-energy band from 300-400 nm was originated from the localized π-π* transition. While the low-energy band in the range of 400-650 nm could be ascribed to the intermolecular chargetransfer (ICT) between electron-rich donor TBF and electron-deficient acceptor TPD, which are similar to the analogue BDT-TPD polymers [8]. The absorption revealed much broader in film state when compared with that in solution. Especially the absorption edge in film state was red-shifted more 100 nm than that in solution, which may indicate the enhancement intermolecular interaction. The optical band gap (E<sub>g</sub>) could be estimated from the onset of absorption in film (E<sub>g</sub> = 1240/λ<sub>onset</sub> eV). Then, optical band-gap of 1.83 eV was calculated for PTBFTTPD.

3.2. Electrochemical properties

The cyclic voltammetry (CV) was used to investigate the electrochemical properties of polymers. Figure 2b shows the CV curve of PTBFTPD. And the onset potential of the 1st oxidation and 1st reduction peaks were 1.05 V and -0.65 V for PTBFTPD. Then HOMO and LUMO energy levels of PTBFTPD could be calculated by using the equation 1 and 2, in which ferrocene was used as an internal reference.
\[ E_{\text{HOMO}} = -e (V_{\text{ox}} + 4.80 - V_{\text{ferro}}) \]  
\[ E_{\text{LUMO}} = -e (V_{\text{red}} + 4.80 - V_{\text{ferro}}) \]  

The HOMO and LUMO energy levels of PTBFTPD were determined to be -5.64 eV and -3.66 eV, respectively. The electrochemical band gap was estimated to 1.98 eV for PTBFTPD. The discrepancies between the electrochemical and optical band gaps might result from the interface barrier between the polymer film and the electrode surface [9]. It is well known that the \( V_{\text{oc}} \) is nearly in direct proportion to the difference between the HOMO level of the polymer and the LUMO level of PC\(_{70}\)BM, therefore the deeper HOMO energy level of PTBFTPD would contribute a higher \( V_{\text{oc}} \) in polymer solar cells [10].

3.3. X-ray diffraction (XRD)

The X-ray diffraction (XRD) method was used to study the molecular stacking behaviour of pure polymer in film state. The grazing incidence XRD pattern of PTBFTPD in the film was displayed in Figure 2c. As shown in the Figure 2c, PTBFTPD shown a strong reflection at 22.5°, due to its (010) plane, corresponding to \( \pi-\pi \) stacking distance (displayed in Figure 2c) of 3.94 Å. The smaller \( d_{\pi-\pi} \) of PBDTTPD would greatly favor charge transport in film state.

3.4. Photovoltaic properties

To investigate the photovoltaic performance of PTBFTPD, the bulk heterojunction PSCs were fabricated using PTBFTPD/PC\(_{70}\)BM blend as the active layer with the device structure of ITO/PEDOT:PSS/active layer/PFN/Al. The detail process was shown in the experimental section. The optimized weight ratio of PTBFTPD and PC\(_{70}\)BM is 1:1.5. It is known that the solvent additive, such as 1,8-diiodooctane (DIO), plays an important role in determining the device performance[11]. Herein, the PTBFTPD devices with various amount of DIO were fabricated. Figure 2d shows the \( J-V \) curves of PTBFTPD/PC\(_{70}\)BM devices at different DIO volume. Finally, a best PCE of 3.00% was obtained with 3 vol% DIO, which may be ascribed to a better morphology formation.

The thermal annealing treatment is also an efficient way to improve the device performance [12]. To study the effect of thermal treatment on the performance of solar cells, PTBFTPD/PC\(_{70}\)BM blend film was heated at different temperature and time before the cathode deposition. And the optimized thermal treatment condition was found to be 100 °C for 30 min. As displayed in Figure 2d, it can see that the PCE of PTBFTPD/PC\(_{70}\)BM device was increased to 4.33%, which is 44% improvement compared to the device without thermal treatment, with the improved \( J_{\text{sc}} \) of 7.51 mA cm\(^{-2}\), a FF of 52.9% and a \( V_{\text{oc}} \) of as high as 1.09 V, that is one of the highest \( V_{\text{oc}} \) in the single bulk heterojunction PSCs.

4. Conclusion

We have designed and synthesized a novel polymer PTBFTPD based on 2D conjugatedalkylthienyl substituted thieno[2,3-f]benzofuran (TBF) and thiopyrroleodione (TPD) unit. The novel polymer possessed a narrow bandgap of 1.83 eV, a deep HOMO energy level (-5.64 eV) and a closer \( \pi-\pi \) stacking. After conventional devices were fabricated using PTBFTPD as donor blending with PC\(_{70}\)BM as acceptor, a power conversion efficiency (PCE) of 4.33% with a high open-circuit voltage (\( V_{\text{oc}} \)) of 1.09 V was obtained. The result indicates the promising potential of thieno[2,3-f]benzofuran unit for high efficient polymer solar cells with a high voltage.

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