



Random copolymers containing tetrafluorophenylene unit with deep HOMO energy levels for solar cell applications



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ABSTRACT

Two Novel terpolymers poly[4,8-di(2-ethylhexyloxy)benzo[1,2-b:4,5-b']dithiophene-3,6-bis-(thiophen-2-yl)-N,N'-bis(2-octyl-1-dodecyl)-1,4-dioxo-pyrrolo[3,4-c]pyrrole-co-2,6-ditetrafluorophenyl-4,8-di(2-ethylhexyloxy)benzo[1,2-b:4,5-b']dithiophene} (PBDT-DPP-TFB) are designed and synthesized as donor materials in PSCs by incorporation of tetrafluorophenylene (TFB) unit with different mole ratio of 1% and 5%, namely PBDT-DPP-TFB1% and PBDT-DPP-TFB5%. It is found that through the introduction of small amount tetrafluorophenylene (TFB) into the BDT-DPP backbone, absorbance range, energy levels, the charge carrier mobility and the device performance are significantly manipulated and enhanced. Lower HOMO energy levels are emphasized for PBDT-DPP-TFB1% (−5.39 eV) and PBDT-DPP-TFB5% (−5.43 eV) compared to pristine PBDT-DPP without TFB unit, due to the strong electron-withdrawing feature of the TFB. Thanks to the more suitable energy levels, and a more favorable morphology with improved excitons dissociation and charge transport in the active layer, the inverted device based on PBDT-DPP-TFB with 1% TFB achieves a dramatic improved PCE of 2.9% with about 200% enhancement to the device with the pristine PBDT-DPP. This work demonstrates the potential of TFB in developing new organic materials for optoelectronic devices, as well as the variation of the third component can be another way to construct D-A polymers with favorable properties.

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1. Introduction

Polymer solar cells (PSCs) as one of promising eco-friendly energy have greatly attracted considerable attention due to their light weight, easy fabrication, and capable of large-scale flexibility [1–3]. Over the recent years, record power conversion efficiencies (PCE) of more than 10% for single-junction structure in the bulk heterojunction (BHJ) PSCs have been successfully achieved [4–6]. This is mainly attributed to the huge optimization of the active layer by both the design of materials and the processing of the blend films [7–10]. Active layer consists of a blend of a polymer electron donor and an electron acceptor (typically fullerene family) based on BHJ structure with a nanometer length scale phase separation. The most important function of donor/acceptor BHJ

blend is to harvest sufficient light, transfers optical energy, form excitons and provide efficient charge dissociation as well as favorable charge transport at interfaces [11–13].

To further achieve PCE of 15% for single junction PSCs predicted in the previous reports, development of highly efficient polymer donors is very desirable to close the gap [14–16]. Donor-acceptor (D-A) type polymers with extended π -conjugation and distinct properties have brought rapidly progress on polymer solar cells (PSCs), due to their tunability of optical absorption, energy level, and carrier mobility [17–19]. Therefore, the state-of-the-art PSCs are predominantly based on D-A polymers of the active layer [20–22]. Among so many superior high performing materials, conjugated polymers based on benzo[1,2-b:4,5-b']dithiophene (BDT) have been already extensively studied. It could be attributed to its highly planar nature, strong absorption and high charge mobility. Up to date, the low band-gap conjugated donor materials reported and affording PSCs with high mobility and impressive PCEs are BDT-based polymers, such as poly[[4,8-bis(2-ethylhexyl)oxy] benzo[1,2-b:4,5-b'] dithiophene-2, 6-diyl][3-fluoro-2-[(2-

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ethylhexyl)carbonyl]thieno[3,4-b]thiophenediyl]] (PTB7) [23]. Great fruits have been made to further improve photovoltaic performance up to 11% by chemical modifications of PTB7 to 2-dimensional PTB7-Th [24]. In addition, BDT block combined with different acceptor fragments, such as thieno[3,4-c]pyrrole-4,6-dione (TPD) [25], benzo[2,1,3]thiadiazole (BT) [26], quinoxaline (DTQx) [27], could afford decent PCE of the devices. However, the D-A copolymer (PBDT-DPP) based BDT and a high performance acceptor segment diketopyrrolo-[3,4-c']pyrrole (DPP) did not achieve a satisfactory device performance, despite its strong light absorption [28,29]. The reported PCE of devices with PBDT-DPP only deliver moderate value. It demonstrates that the low open circuit voltage (V_{oc}) limit the performance enhancement, due to the high HOMO of PBDT-DPP [30]. In principle, the V_{oc} of devices is proportional to the energy difference between the HOMO level of electron donor (polymers) and the lowest unoccupied molecular orbital (LUMO) energy level of acceptors [31]. Therefore, high V_{oc} would be directly obtained through decreasing the HOMO levels of donor polymers or enlarging the LUMO levels of acceptors. And increased efforts have been devoted to tailor the HOMO and the LUMO then to boost the photovoltaic performance.

Some strategies have been devoted to reduce the band gap and modulate energy levels of organic semiconductors. Introduction into conjugated backbones with quinoid structures [32] and strong electron-donating groups such as alkoxy [33] or electron-withdrawing groups [34] (fluorine atom) have been successfully applied. Polymers based on two donors and one acceptor or one donor and two acceptors by ternary copolymerization have been proved to provide another promising route. Compared to the conventional two component donor polymers, the newly terpolymers consisted of three different monomers could fine-tune the energy levels for the improvement of the coverage of the solar spectrum and higher open-circuit voltage [35]. Among our previous work, we have successfully attempted to apply a novel A-D1-A-D2 structure to decrease the HOMO levels of polymers [36].

Recently, tetrafluorophenylene (TFB) has been found to be a promising candidate for designing novel donor polymers. The fluorine (F) atom has unique properties [37–39]: i) the strong electronegativity distinctly reduces both HOMO and LUMO energy level; ii) the small atom size may not cause steric hindrance to the molecular packing; iii) the interaction between C-F and H-C in compounds may promote molecular organization and crystallization, which may enhance the charge-carrier mobility. The polymers based on TFB have already frequently been used for organic field-effect transistors (OFETs) as p-channel or n-channel materials [40], whereas it has not been widespread-employed for OPVs. Nonetheless, these remarkable findings attract us to explore the potential utility of the TFB as a structural platform to build novel polymers applied for OPVs. In view of this, if introducing TFB segment into the backbone of PBDT-DPP, the HOMO levels, charge mobility as well as the final photovoltaic performance of the devices are expected to be improved.

In consideration of the strong electron-withdrawing features and relative low solubility of TFB as well as keeping the building structure of PBDT-DPP, only a small amount of TFB (1 wt% and 5 wt%) is incorporated into backbone to afford two random terpolymers, namely, poly{4,8-di(2-ethylhexyloxy)benzo[1,2-b:4.5-b']dithiophene-3,6-bis-(thiophen-2-yl)-N,N'-bis(2-octyl-1-dodecyl)-1,4-dioxo-pyrrolo[3,4-c]pyrrole-co-2,6-ditetrafluorophenyl-4,8-di(2-ethylhexyloxy)benzo[1,2-b:4.5-b']dithiophene} (PBDT-DPP-TFB1%) and PBDT-DPP-TFB5%. We expect that the optical and electrical properties of the resultant polymers and the blend morphology of the active layer can be greatly improved by a tiny chemically structural modification. Moreover, the corresponding alternating polymer poly{4,8-di(2-ethylhexyloxy)benzo[1,2-

b:4.5-b']dithiophene-3,6-di-(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione}(PBDT-DPP) is also prepared, and the comparison between the random and alternating polymer on photoelectric properties has been systemically conducted.

2. Experimental

2.1. Materials

All raw material{monomers 2,6-bis(trimethylstannyl)-4,8-di(2-ethylhexyloxy)benzo[1,2-b:4.5-b']dithiophene (BDT) and 3,6-bis(5-bromo-thiophen-2-yl)-N,N'-bis(2-octyl-1-dodecyl)-1,4-dioxopyrrolo[3,4-c]pyrrole (DPP), 1,4-diiodotetrafluorobenzene (TFB)} and reagents were purchased from commercial sources and used without further purification.

2.2. General measurement and characterization

^1H NMR spectra was recorded in deuterated solvents on a Bruker ADVANCE 600 NMR Spectrometer. ^1H NMR chemical shifts were reported in ppm downfield using deuterated chloroform as solvent. Molecular weights of the polymers were determined using Waters 2410 gel permeation chromatograph (GPC) in tetrahydrofuran (THF). The working temperature was 40 °C and the concentration of the samples was a mass of 2.0–2.5 mg mL⁻¹. Thermo gravimetric analysis (TGA) was performed on a TA-600 for thermal analysis at a heating rate of 10 °C/min under nitrogen with a weight of 5 mg. Ultraviolet-visible (UV-vis) absorption spectra were measured with Perkin Elmer Lambda 750 UV-vis spectrophotometer. Cyclic voltammetry (CV) was performed with a Zahner IM6e electrochemical workstation in an electrolyte solution of 0.1 M tetrabutylammonium hexafluorophosphate in acetonitrile. The UPS measurement was carried out in a Thermo-VG Scientific ESCALAB 250 using a He I (21.22 eV) discharge lamp. X-ray diffraction (XRD) study of polymers was carried out on a Bruker D8 Focus X-ray diffractometer operating at 30 kV and 20 mA with a copper target ($\lambda = 1.54 \text{ \AA}$) and at a rate of 1°/min. Current-voltage (J-V) characteristics were recorded using a Keithley 2400 Source Meter in the dark under 100 mW/cm² simulated AM 1.5 G irradiation. The incident photon-to-current conversion efficiency (IPCE) spectrum was detected under monochromatic illumination (Oriol Cornerstone 260 1/4 m monochromator equipped with Oriol 70613NS QTH lamp). The thicknesses of the active layer were determined by the Atomic-Profiler. Atomic force microscopic (AFM) image was measured with a Nanoscope III A scanning probe microscope using the tapping mode. The thin film morphology floated onto the Cu grid was characterized by transmission electron microscopy (TEM) with a JEOL 2000 FX MARK II operating at 200 kV. Time-resolved photoluminescence were carried out by an Edinburgh Instruments FLS920 spectrometer.

2.3. The synthesis procedures

2.3.1. Synthesis of 3,6-bis(5-bromothiophen-2-yl)-2,5-bis(2-ethylhexyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (Br2-DPP)

N-bromosuccinimide (NBS) (0.34 g, 1.91 mmol) 2,5-bis(2-ethylhexyl)-3,6-di(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (DPP) (0.5 g, 0.95 mmol), chloroform (40 mL) were added to a 100 mL round-bottom flask. The mixture was stirred at room temperature under dark for about 1 h and then extracted with water (50 mL × 3). The combined extracts was then dried with anhydrous MgSO₄ and evaporated. The crude product was purified by flash column chromatography (eluent: ethyl acetate: hexane = 1:1, volume ratio) to give a pure product as a bright red solid (0.41 g, 82%). ^1H NMR (400 MHz, CDCl₃), δ : 8.65 (d 2H), 7.32 (d 2H), 3.92 (t 4H), 1.86 (t 2H), 1.42–1.18 (m 16H), 0.94–0.81 (m 12H).

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