

A narrow-bandgap donor polymer for highly efficient as-cast non-fullerene polymer solar cells with a high open circuit voltage

Chunmei Chang, Wanbin Li, Xia Guo^{**}, Bing Guo, Chennan Ye, Wenyan Su, Qunping Fan, Maojie Zhang^{*}

Laboratory of Advanced Optoelectronic Materials, College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou, 215123, China

ARTICLE INFO

Keywords:

Non-fullerene polymer solar cells
Narrow-bandgap copolymer
Fluorine substituents

ABSTRACT

A new narrow-bandgap copolymer **PBFTT**, based on 4,8-bis(5-(2-ethylhexyl)-4-fluorothiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene (BDT-2F) as donor unit and octyl-3-fluorothiopheno[3,4-b]thiophene-2-carboxylate (TT) as acceptor unit, was synthesized as donor material for non-fullerene (NF) polymer solar cells (PSCs) application. Compared to the analogue polymer PTB7-Th, **PBFTT** with two fluorine atoms in the conjugated side chains of BDT possesses a deeper HOMO energy level of -5.47 eV and a slightly enhanced hole mobility of $3.13 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ versus (vs.) a HOMO energy level of -5.30 eV and a hole mobility of $1.11 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for PTB7-Th. Hence, the corresponding PSCs based on **PBFTT**:ITIC exhibited an optimal PCE of 9.1% with a V_{oc} of 0.94 V, a J_{sc} of 16.0 mA cm^{-2} , and a FF of 60.5% compared to a PCE of 6.8% with a V_{oc} of 0.81 V, a J_{sc} of 14.2 mA cm^{-2} and a FF of 59.1% for PTB7-Th:ITIC-based PSCs. Notably, this PCE is among the highest values for the NF-PSCs based on narrow-bandgap polymer without extra treatments. These results indicate that **PBFTT** is a promising narrow-bandgap polymer donor material for NF-PSCs application.

1. Introduction

Polymer solar cells (PSCs) are considered as a promising solar technology owing to their low cost, light weight, and potential for making large-area and flexible devices through roll-to-roll processing [1–6]. A typical bulk-heterojunction (BHJ) PSCs contains a p-type conjugated polymer as donor and an n-type organic semiconductor (n-OS) as acceptor. For the n-OS acceptors, fullerene derivatives [7] have been the dominant acceptor materials in past two decades and fullerene-based PSCs have achieved power conversion efficiencies (PCEs) of over 10% [8–12]. However, fullerene derivatives exhibit many intrinsic drawbacks, such as costly preparation and purification, weak absorption in the visible region, limited energy level variability, and poor morphology stability. Recently, the non-fullerene (NF) acceptors are gradually emerging as competitors because of their advantages of easy synthesis, strong absorption in the visible region, tunable energy levels, and good morphology stability [13–19]. Furthermore, the PSCs based on a polymer donor and a small molecule acceptor (SMA) have made rapid development in the past two years, mainly due to the intensive research on the design and synthesis of the new SMA materials [20–37] and wide-bandgap polymers [38–48]. However, the exploration of narrow-bandgap polymer donor materials for NF-PSCs

application is still rare [38].

Modulation of molecular energy level is one of the most important topics in the design of polymer donor materials [49–55]. As we know, the open circuit voltages (V_{oc}) of PSCs are roughly directly proportional to the gaps between the highest occupied molecular orbit (HOMO) energy levels of the donor materials and the lowest unoccupied molecular orbit (LUMO) energy levels of the acceptor materials in the active layers [56], and therefore, V_{oc} can be effectively improved by elevating the LUMO energy levels of the acceptors or decreasing the HOMO energy levels of the donors [57–59]. Furthermore, the polymers also should possess matched HOMO and LUMO energy levels with the acceptor materials for the efficient excitons dissociation [60–62]. Recently, fluorination has attracted considerable attention due to its multiple synergistic effects on the energy levels, absorption and carrier transport properties of the polymers [63–68]. In our previous work, it has been found that attaching two fluorine atoms to the side chain of alkylthienyl substituted benzodithiophene unit (BDT-T) in D-A polymers could make the HOMO energy levels of the related polymers significantly downshift and hence the V_{oc} of the related PSCs has been effectively improved [63]. Hence, the device performance was impressively promoted.

Hence, in this work, we synthesized a new copolymer **PBFTT** based

* Corresponding author.

** Corresponding author.

E-mail addresses: guoxia@suda.edu.cn (X. Guo), mjzhang@suda.edu.cn (M. Zhang).

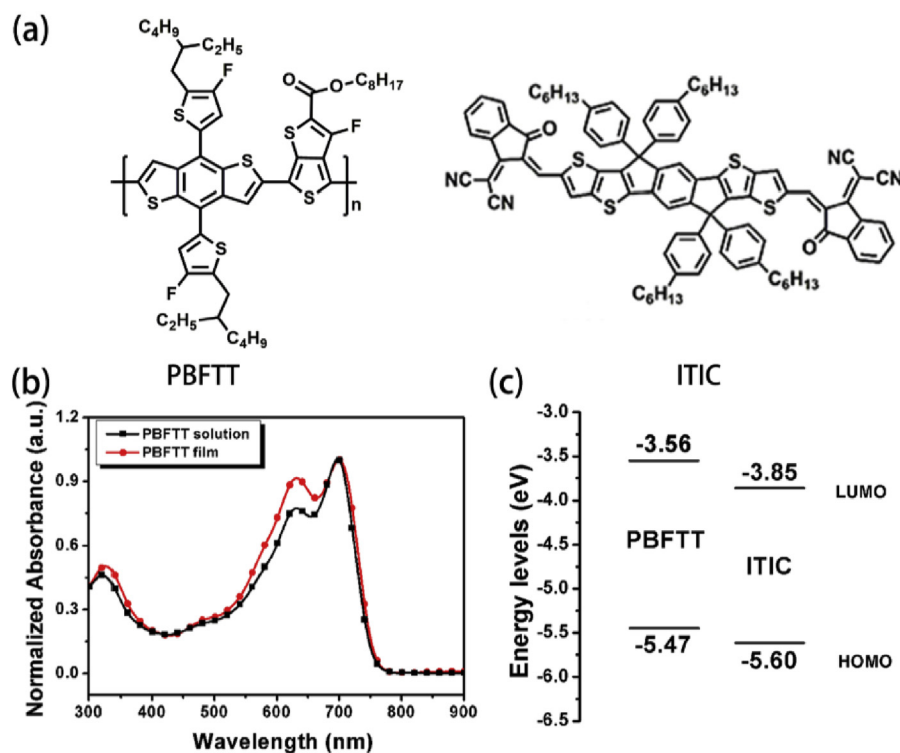


Fig. 1. (a) Chemical structures of PBFTT and ITIC. (b) Absorption spectra of PBFTT in solution and film. (c) Energy level diagrams for PBFTT and ITIC.

on 4,8-bis(5-(2-ethylhexyl)-4-fluorothiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene (BDT-2F) as donor unit and octyl-3-fluorothiopheno[3,4-*b*]thiophene-2-carboxylate (TT) as acceptor unit, as shown in Fig. 1a. The optical, electrochemical and photovoltaic properties, the molecular packing and the morphology of the blend films were investigated. Compared with the analogue polymer PTB7-Th [69], PBFTT exhibits a similar absorption spectrum with slight blue-shift, while it possesses a deeper HOMO energy level of -5.47 eV and a slightly enhanced hole mobility of $3.13 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ vs. a HOMO energy level of -5.30 eV and a hole mobility of $1.11 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for PTB7-Th. The PSCs based on PBFTT:ITIC showed a higher PCE of 9.1% with a V_{oc} of 0.94 V, a short-circuit current density (J_{sc}) of 16.0 mA cm^{-2} , and a fill factor (FF) of 60.5% in comparison with the PCE of 6.8% for PTB7-Th:ITIC-based devices (a V_{oc} of 0.81 V, a J_{sc} of 14.2 mA cm^{-2} , and a FF of 59.1%). Notably, this PCE is among the highest values for the NF-PSCs based on narrow-bandgap polymer without extra treatments. These results indicate that PBFTT is a promising narrow-bandgap polymer donor material for NF-PSCs application.

2. Results and discussion

The synthetic route of PBFTT is shown in Scheme S1 of Supporting Information (SI). PBFTT was synthesized using a Pd-catalyzed Stille-coupling reaction. The polymer exhibits good solubility in chloroform, chlorobenzene, and *o*-dichlorobenzene. The number average molecular weight (M_n) and polydispersity index (PDI) of PBFTT were 42.58 K and 1.88, respectively, measured by gel-permeation chromatography (GPC) with 1,2,4-trichlorobenzene as the solvent and polystyrene as a standard at a high temperature of 160°C . Thermogravimetric analysis (TGA) was measured to evaluate the thermal stability of PBFTT, and the corresponding TGA plot is displayed in Fig. S1 of SI. The onset of decomposition temperature (T_d) at 5% weight loss is ca. 350°C , indicating the thermal stability of the polymer is good enough for the PSCs application.

Fig. 1b shows the UV-vis absorption spectra of PBFTT in chloroform solution and solid film. In solution, PBFTT exhibits strong absorption in

the region of 300–400 nm and 500–750 nm, which can be ascribed to the π - π^* transitions of the backbone and intra-molecular charge-transfer of the polymer respectively, accompanied by a maximum absorption peak at 698 nm. In the solid film, the maximum absorption peak is slightly red-shifted to 700 nm. As shown in Fig. S2a of SI, compared with PTB7-Th, the absorption spectrum of PBFTT exhibits a slight blue-shift with an optical bandgap (E_g^{opt}) of 1.64 eV vs. 1.57 eV for PTB7-Th.

The electrochemical cyclic voltammetry (CV) was shown in Fig. S2b, which was exhibited to measure the HOMO and LUMO energy levels of the polymer. The onset oxidation potentials (φ_{ox}) of PBFTT is 0.76 V vs. Ag/Ag⁺, while its onset reduction potentials (φ_{red}) is -1.15 V vs. Ag/Ag⁺, respectively. The HOMO and LUMO energy levels of PBFTT are -5.47 eV and -3.56 eV (Fig. 1c), according to formula [70]: HOMO = $-e(\varphi_{ox} + 4.71)$ (eV) and LUMO = $-e(\varphi_{red} + 4.71)$ (eV). The HOMO and LUMO energy levels of PTB7-Th are -5.30 eV and -3.33 eV [69]. Obviously, the HOMO energy level of PBFTT decreased by 0.17 eV as a result of the electrophilic ability of fluorine substituents, which helps to realize higher V_{oc} in PSCs. In addition, the ΔE_{LUMO} between the donor and acceptor in the PBFTT:ITIC blend are 0.29 eV (see Fig. 1c), which is sufficient for exciton dissociation and charge transfer between the donor and acceptor [60,61].

The crystallinity and molecular packing of the polymer film were measured by the X-ray diffraction (XRD). The XRD pattern of pure PBFTT film is displayed in Fig. 2. It exhibits a clear and strong (100) diffraction peaks at $2\theta = 4.4^\circ$, corresponding to a *d*-spacing of 20.1 Å, arising from the ordered alkyl side chain packing. Meanwhile, it also shows a pronounced diffraction peak at $2\theta = 23.7^\circ$, corresponding to the (010) π - π stacking with a smaller *d*-spacing of ~ 3.8 Å than that of PTB7-Th (~ 3.9 Å) [69], which is more favorable for the charge transport.

To investigate the photovoltaic properties of PBFTT, the NF-PSCs were fabricated with an inverted device structure of ITO/ZnO/PFN/PBFTT:ITIC/MoO₃/Al. Firstly, the influence of the donor/acceptor (D/A, PBFTT:ITIC) weight ratios (w/w) in the active layer on device performance was investigated. Fig. 3a shows the current density–voltage

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