Air-processed high performance ternary blend solar cell based on PTB7-Th:PCDTBT:PC₇₀BM

Xiaoxiang Sun, Jian Ni*, Chang Li, Like Huang, Rui Xu, Zhenglong Li, Hongkun Cai,
Juan Li, Jianjun Zhang**

College of Electronic Information and Optical Engineering, Nankai University,

The Tianjin Key Laboratory for Optical -Electronics Thin Film Devices and
Technology, Tianjin, 300071, China.

*Corresponding author. E-mail address: elsevier_jianni@163.com.

**Corresponding author. E-mail address: jjzhang@nankai.edu.cn.

Abstract: Ternary bulk heterojunctions (BHJs) are promising candidates that can improve the power conversion efficiencies (PCEs) of organic solar cells (OSCs). In this paper, a ternary OSC with two donors, including one wide bandgap polymer poly[N-9'-heptadecanyl-2,7-carbazole-alt-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)] (PCDTBT), one low bandgap polymer Poly[4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-co-3-fluorothieno[3,4-b]thiophene-2-carboxylate] (PTB7-Th), and one acceptor [6,6]-phenyl C70 butyric acid methyl ester (PC₇₀BM), is fabricated in atmospheric conditions. By incorporating a 20% content of PCDTBT, an optimized PCE of 7.86% for ternary OSC is characterized by a short-circuit current density (J_{sc}) of 15.21 mA cm⁻², a fill factor of 69.70% and an open-circuit voltage (V_{oc}) of 0.74 V. The V_{oc} values increased steadily from 0.73 to 0.86 V as the increase of PCDTBT fraction, which indicates that the V_{oc} of ternary OSC is not limited by the smallest one of the corresponding binary OSC. We show that the J_{sc} of the ternary OSC is better than those of the binary OSC in virtue of the complementary polymer absorption and cascade energy levels, as well as optimized morphology of the ternary system. Furthermore, the lifetime of the devices with PCDTBT is greatly enhanced. This work indicates that two donors (PTB7-Th/PCDTBT) ternary BHJs system provide a simple and effective method to improve the performance and also the stability of OSCs.

Key words: ternary organic solar cells; low bandgap polymer; wide bandgap polymer; cascade energy levels; morphology; stability

1. Introduction

Organic solar cells (OSCs) have made great progress recently and have shown their potential in low-cost, flexible, and lightweight solar energy conversion devices [1-2]. Although OSCs have such advantages, a further increase of their power conversion efficiency (PCE) and stability is needed for future applications. Nowadays, lots of strategies have been developed to enhance the PCE of OSCs based on different principles, such as synthesizing of new low bandgap polymers with improved optical absorption properties [3-9], optimizing device morphology [10-12], using effective interlayer [13-14], using of surface plasmon resonance effect [15-19], and developing of new device architecture [20-22]. To further increase the PCE of single-junction devices, the novel concept of ternary blend systems which typically contain two donor materials and one fullerene acceptor have been proposed [23], it is an attractive strategy to overcome the PCE bottleneck for binary devices while maintaining the simplicity of the processing conditions used for single active layer devices rather than the more complex tandem cells. Owing to the nature of the bulk heterojunction structure employed in most of the organic solar cells, additional polymers [24-26], small molecules [27], quantum dots [28], or fullerene derivatives [29-30] can simply be mixed into the conventional binary layer, resulting in a more efficient ternary system with broad-band light harvesting.

Admittedly, appropriate selection of the third components is one of the critical factor for the ternary system, not just take into account the complementary absorption spectrum and appropriate energy level, but the third components also must show good miscibility with the electron donor and electron acceptor materials in order to control the domain size of the ternary blend for efficient exciton dissociation. Meanwhile,

stability is also one of the major hurdles that must be tackled for the ternary OSCs. Previous researches have shown that both of the structure and composition of the OSCs would exercise influence on the stability of OSCs. Mc Gehee et al. show cased a PCDTBT-based PSC rigid device with a lifetime of seven years [31]. Therefore, a study on the new ternary system is of great importance to further increase the efficiency and the stability.

In this paper, a ternary bulk heterojunction system, consisting of the wide bandgap polymer poly[N-9'-heptadecanyl-2,7-carbazole-alt-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)] (PCDTBT), the low bandgap polymer Poly[4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-co-3-fluorothieno[3,4-b]thiophene-2-carboxylate] (PTB7-Th) and the electron acceptor [6,6]-phenyl C70 butyric acid methyl ester (PC₇₀BM), was designed and fabricated. PCDTBT is selected as the third component because of complementary absorption spectrum, appropriate energy level, good miscibility and good air stability [32]. The PCE of the ternary OSCs (7.86%) is higher than that of binary systems based on the low bandgap polymer (6.91%) or wide bandgap polymer (2.74%).

2. Experiment

2.1 Solar cell fabrication

All devices were fabricated and characterized in air, without protecting environment. Binary and ternary OSCs were fabricated with inverted structure of ITO/ZnO/active layer/WO₃/Ag, as shown in **Fig. 1a** [33-34]. The energy level diagrams for PCDTBT, PTB7-Th, and PC₇₀BM was shown in **Fig. 1b**. The polymers and PC₇₀BM (1:1.5 w/w) were co-dissolved in the mixed solvent of chlorobenzene and 1,8-diodooctane (97:3 vol/vol). The overall polymer concentration was 10 mg

ml⁻¹ and the solution was stirred at 90 °C for 12 h under an atmosphere environment. ITO glass substrate was cleaned in detergent, water, acetone, and isopropyl alcohol under ultrasonication for 15 min and then exposed to ultraviolet ozone irradiation for 20 min. A thin-layer (~30 nm) ZnO was spin-coated onto the cleaned ITO surface and subsequently dried at 200 °C for 1 h in air. Then the active layer was spin-coated on the ZnO layer using the as-prepared solutions at 2,000 rpm for 30s in air. Finally, a 7-nm thick WO₃ layer and a 100-nm thick Ag layer were subsequently evaporated through a shadow mask (active area 6 mm²) under the pressure of 7.0×10⁻⁴ Pa.

2.2 Measurements

The current density-voltage (*J-V*) characteristics of the devices were measured at 25°C under 1-sun (AM 1.5G, 100 mW/cm²) simulator radiation. The absorption spectra of active layers were measured by spectrophotometer (Cary 5000 UV-VIS). Transmission electron microscopy (TEM) images were obtained using a Tecnai G² F20, the active layer on a PEDOT:PSS substrate was removed by dipping in DI water and then a holey carbon-coated copper grid was used to hold the film, which was dried in an oven at 50 °C. The hole mobility was measured via the space charge limited current (SCLC) method by using a device architecture of ITO/PEDOT:PSS/active layer/Au by acquiring the Current–Voltage curves and fitting the results to a space-charge limited form. The thicknesses of the active layers were measured by using a step profilometer (AMBIOS-XP2). Photoluminescence (PL) was used to measure the emission spectra of the blend films.

3. Results and discussion

The J - V characteristics of the devices with different contents of PCDTBT are shown in **Fig. 2a**. The devices parameters are summarized in **Table 1**. The overall polymer to PC₇₀BM ratio was kept at 1:1.5 in this work. The weight percentages of the added PCDTBT were controlled to be 10%, 20%, 30%, 50% and 70%, respectively. To evaluate the effect of the additive, PTB7-Th:PC₇₀BM and PCDTBT:PC₇₀BM binary control devices were also fabricated and characterized under the same conditions. The PTB7-Th:PC₇₀BM used as a reference device give a PCE of 6.91% with an open circuit voltage (V_{oc}) of 0.73 V, a short circuit current density (J_{sc}) of 13.74 mA cm⁻² and a fill factor (FF) of 68.53%. Meanwhile, the V_{oc} of the ternary blend solar cells is increased with the increase of PCDTBT content because PCDTBT have deeper energy levels than PTB7-Th. It is likely that the increased V_{oc} with higher PCDTBT contents is from the electronic alloy charge state, as shown in **Fig. 3a**. This phenomenon is also observed for many other ternary systems reported [35-38]. On the other hand, it is clear from **Fig. 2a** that the J_{sc} is significantly enhanced after the incorporation of a small amount of PCDTBT (10% or 20%) into the active layer. By adding 20% of PCDTBT into the host binary blend, PCE is enhanced to 7.86% with a J_{sc} of 15.21 mA cm⁻², V_{oc} of 0.74 V, and FF of 69.70%. The dark J - V curves (inset, Fig. 2a) suggest similar injection and extraction behavior in the PTB7-Th:PC₇₀BM and PTB7-Th:PCDTBT:PC₇₀BM (0.8:0.2:1.5) devices. However, a further increase of the amount of PCDTBT leads to the decrease of performances, as shown in Fig. 3. The low performances of devices with high PCDTBT contents are expected since the DIO additive is usually not required to the optimal processing of PCDTBT devices. Here, the PCDTBT:PC₇₀BM devices with and without DIO show the PCE of 2.74% and 4.39%, respectively. The external quantum efficiency (EQE) of ternary devices was subsequently conducted to better

illuminate the enhancement of the devices performance, as shown in **Fig. 2b**. The EQE values are enhanced in the wavelength region between 500 to 680 nm, which can be mostly ascribed to the enhanced light absorption of PCDTBT, as shown in **Fig. 2c**. The device that added to 20% PCDTBT shows the maximum EQEs. The small amount of PCDTBT play the role of a hole relay between PC₇₀BM and PTB7-Th via its appropriate HOMO orbital. The HOMO energy level of PCDTBT is between PTB7-Th and PC₇₀BM, forming cascade HOMO energy levels for more effective extraction of holes from PC₇₀BM (**Fig. 1b**) [23]. To prove this, we measured the film PL of PCDTBT, PTB7-Th, and PTB7-Th:PCDTBT (0.8:0.2) excited at 610 nm, as shown in **Fig. 2d**. The pure PCDTBT film shows a strong emission, while PTB7-Th exhibits a weak photoluminescence emission signal with a peak at 760 nm. The photoluminescence of PCDTBT is completely quenched while the photoluminescence of PTB7-Th remained almost the same in the PTB7-Th:PCDTBT blend film (0.8:0.2). This results indicate that photo-induced electron transfer from PTB7-Th to PCDTBT (hole transfer from PCDTBT to PTB7-Th) exists. On the other hand, hole transfer from PC₇₀BM to PCDTBT has already been demonstrated by a 2.74% device performance for PCDTBT:PC₇₀BM, which indicates holes could transfer from PC₇₀BM to PCDTBT and finally to PTB7-Th. We also fabricated a solar cell using a mixture of PTB7-Th and PCDTBT in a 1:1.5 ratio and achieved a PCE of 0.013% (V_{oc} = 0.38 V, J_{sc} = 0.132 mA cm⁻² and FF = 25.4%). Although the PCE was poor, the result proved that charge separation and transport between PTB7-Th and PCDTBT occur at their interfaces.

In order to characterize the influence of PCDTBT on carrier transport in the OPVs, hole-only devices with device structure of ITO/PEDOT:PSS/active layer/Au were prepared, as shown in **Fig. 4a**. The hole mobilities of the devices with different

percentage of PCDTBT are summarized in **Table 2**. The curves can be fitted with the SCLCs given by the Murgatroyd equation [39-40]. Hole mobility increased from $5.32 \times 10^{-4} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ (PTB7-Th:PC₇₀BM) to $5.94 \times 10^{-4} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ (PTB7-Th:PCDTBT:PC₇₀BM, 0.9:0.1:1.5) and finally to $6.21 \times 10^{-4} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ (PTB7-Th:PCDTBT:PC₇₀BM, 0.8:0.2:1.5). However, a further increase of the amount of PCDTBT leads to the decrease of hole mobility. The improved hole mobilities helped to explain the better J_{sc} and FF in the ternary system, as shown in **Fig. 3** and **Fig. 4**.

To study the influence of the morphology by adding PCDTBT to PTB7-Th, the transmission electron microscopy (TEM) micrographs for approximately 100-nm-thick active layer films with the content of PCDTBT of 0%, 10%, 20% and 30% were investigated. As shown in **Fig. 5**, the bright and dark regions in the TEM images correspond to the donors and PC₇₀BM rich domains, respectively [41-42]. Both PTB7-Th:PCDTBT:PC₇₀BM (0.9:0.1:1.5) blend film (**Fig. 5b**) and PTB7-Th:PCDTBT:PC₇₀BM (0.8:0.2:1.5) blend film (**Fig. 5c**) show fibrous features, however, no such structure is observed in the PTB7-Th:PC₇₀BM (**Fig. 5a**). This result indicates that the PCDTBT plays a key role in the formation of fibrous structure. In previous reports, the fine dispersed fibrils have been found beneficial to the process of exciton separation and charge transport [43-44]. As the further increase the percentage of PCDTBT, the phase separation size became larger than before (**Fig. 5d**). The large degree of phase separation limited the exciton dissociation, resulting in poor device performance.

The stability of ternary and binary solar cells was compared by storing the devices in ambient air, and periodically testing their photovoltaic performances. As shown in **Fig. 6**, after 7 days of storage in air, the ternary solar cells PTB7-

Th:PCDTBT:PC₇₀BM (0.8:0.2:1.5) retain 70% of their initial value of PCE, while the binary solar cells PTB7-Th:PC₇₀BM (1:1.5) degrade to 44%. To further study the effect of the third component PCDTBT on the air stability of the active layer, we compared the degradation process of PTB7-Th:PC₇₀BM and PTB7-Th:PCDTBT:PC₇₀BM films stored in air at ambient temperature and humidity. The morphology of the active layers was investigated by AFM. As shown in **Fig. 7**, a few defects can be observed in the as-prepared binary and ternary active layers, however, several distinct defects with different sizes can be discovered both in the binary and ternary active layers after 7 days storing in air, which can certainly lead to the degradation of devices performance. Admittedly, for the active layer with DIO as the solvent additive, the DIO may be residual due to its high boiling point. It is reported that DIO molecules are highly sensitive to light and can directly saturate the polymer conjugated backbone or be trapped by the fullerene moieties, which may result to the instability of OSCs [45-46]. Meanwhile, oxygen and water always easily diffuse into the device in ambient air and limit the stability of OSCs [47-48]. Furthermore, as shown in **Fig. 6**, the stability of ternary solar cells is obviously much better than binary solar cells. In the ternary PTB7-Th:PCDTBT:PC₇₀BM (0.8:0.2:1.5) active layer, the number of defects is less than that of binary PTB7-Th:PC₇₀BM active layer after 7 days. Here we infer that the improved stability of ternary device maybe attribute to the existence of PCDTBT to some extent, since the HOMO level of the PCDTBT is below the air oxidation threshold of 5.27 eV, which ensures better air-stability [32,49]. In short, ternary OSCs have great potential for obtaining high-performances and stability.

4. Conclusion

In summary, we fabricated ternary blend BHJ solar cells containing PTB7-Th and PCDTBT as the donors and PC₇₀BM as acceptor. A PCE of 7.86% was achieved with 20% of PCDTBT incorporation, which was the combined effects of a complementary light harvesting, energy level cascading, enhanced hole mobility and optimized device morphology. The V_{oc} of the ternary blends solar cells was enhanced with the increase of PCDTBT content since the deeper HOMO energy levels of PCDTBT compared with PTB7-Th. Furthermore, the stability of the ternary devices was improved to a certain extent compared with the binary devices. These results indicate that the use of ternary blend BHJ solar cells is an effective strategy to overcome the predicted ultimate efficiencies for binary blend photovoltaic devices, as they can exhibit potentially higher attainable J_{sc} , V_{oc} products through judicious component selection and compositional control without sacrificing the attractive simplicity of processing in single-active-layer BHJ solar cells.

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Figure captions

Fig. 1(a) Device structure of the ternary solar cell (glass substrate/ITO/ZnO/PTB7-Th:PCDTBT:PC₇₀BM/WO₃/Ag). (b) Energy level diagrams for PCDTBT, PTB7-Th, and PC₇₀BM.

Fig. 2(a) Current density–voltage characteristics of ternary solar cells with different percentage of PCDTBT. Inset curves shows the dark Current density–voltage characteristics of PTB7-Th:PC₇₀BM and PTB7-Th:PCDTBT:PC₇₀BM (0.8:0.2:1.5) devices. (b) External quantum efficiency (EQE) curves of ternary solar cells with different percentage of PCDTBT. (c) Absorption spectra of PTB7-Th, PCDTBT and PC₇₀BM. (d) Photoluminescence spectra of PCDTBT, PTB7-Th:PCDTBT (0.8:0.2) and PTB7-Th films excited at 610 nm.

Fig. 3(a) The short circuit current density (J_{sc}) and open circuit voltage (V_{oc}) of the OSCs for different percentage of PCDTBT. (b) The PCE of the OSCs for different percentage of PCDTBT.

Fig. 4(a) Hole-only devices based on PTB7-Th:PCDTBT:PC₇₀BM films with different percentage of PCDTBT. (b) The short circuit current density (J_{sc}) and hole mobilities (μ_h) of the OSCs for different percentage of PCDTBT.

Fig. 5 Transmission electron microscopy (TEM) characterization of the ternary devices. (a) TEM image of PTB7-Th:PC₇₀BM. (b) TEM image of PTB7-Th:PCDTBT:PC₇₀BM (0.9:0.1:1.5). (c) TEM image of PTB7-Th:PCDTBT:PC₇₀BM (0.8:0.2:1.5). (d) TEM image of PTB7-Th:PCDTBT:PC₇₀BM (0.7:0.3:1.5).

Fig. 6 The stability of the devices with different percentage of PCDTBT.

Fig. 7 AFM images of binary PTB7-Th:PC₇₀BM active layer (a, c) and ternary PTB7-Th:PCDTBT:PC₇₀BM (0.8:0.2:1.5) active layer (b, d) stored at ambient.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Table 1 Photovoltaic parameters for PTB7-Th:PCDTBT:PC₇₀BM devices with different weight ratios of PCDTBT

PTB7-Th:PCDTBT:PC ₇₀ BM	J_{sc} (mA cm ⁻²)	V_{oc} (V)	FF (%)	PCE (%)
1:0:1.5	13.74(13.41±0.69)	0.73(0.73±0.02)	68.53(65.36±3.15)	6.91(6.35±0.27)
0.9:0.1:1.5	14.51(14.27±0.68)	0.74(0.73±0.02)	69.03(65.71±2.83)	7.38(6.83±0.37)
0.8:0.2:1.5	15.21(14.79±0.58)	0.74(0.74±0.02)	69.70(67.12±2.31)	7.86(7.34±0.24)
0.7:0.3:1.5	13.29(13.07±0.45)	0.74(0.74±0.02)	66.37(64.68±2.03)	6.55(6.25±0.17)
0.5:0.5:1.5	12.18(11.98±0.48)	0.79(0.78±0.02)	63.95(62.03±1.41)	6.13(5.81±0.26)
0.3:0.7:1.5	11.22(11.08±0.67)	0.80(0.80±0.02)	59.84(56.77±3.49)	5.34(5.04±0.25)
0:1:1.5	7.94(7.63±0.47)	0.86(0.86±0.02)	40.28(39.93±2.46)	2.74(2.62±0.11)

Table 2 Hole mobility of PTB7-Th:PCDTBT:PC₇₀BM films with different percentage of PCDTBT.

PTB7-Th:PCDTBT:PC ₇₀ BM	Hole mobility (cm ² V ⁻¹ s ⁻¹)
1:0:1.5	5.32×10 ⁻⁴
0.9:0.1:1.5	5.94×10 ⁻⁴
0.8:0.2:1.5	6.21×10 ⁻⁴
0.7:0.3:1.5	4.88×10 ⁻⁴
0.5:0.5:1.5	4.54×10 ⁻⁴
0.3:0.7:1.5	3.92×10 ⁻⁴
0:1:1.5	2.93×10 ⁻⁴

Graphical abstract