RESEARCH ARTICLE

Effects of BTA2 as the third component on the charge carrier generation and recombination behavior of PTB7:PC₇₁BM photovoltaic system

Leijing Liu¹, Hao Zhang¹, Bo Xiao², Yang Liu¹, Bin Xu¹, Chen Wang³, Shanpeng Wen³, Erjun Zhou², Gang Chen⁴, Chan Im⁵, Wenjing Tian (🖂)¹

1 State Key Laboratory of Supramolecular Structures and Materials, Jilin University, Changchun 130012, China

2 CAS Key Laboratory of Nanosystem and Hierarchical Fabrication, CAS Center for Excellence in Nanoscience, National Center for Nanoscience and Technology, Beijing 100190, China

3 State Key Laboratory on Integrated Optoelectronics and College of Electronic Science & Engineering, Jilin University, Changchun 130012, China 4 Key Laboratory of Physics and Technology for Advanced Batteries, Ministry of Education, Jilin University, Changchun 130012, China

5 Department of Chemistry, Konkuk University, Seoul 05029, Republic of Korea

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Abstract Effects of a benzotriazole (BTA)-based small molecule, BTA2, as the third component on the charge carrier generation and recombination behavior of poly [[4,8-bis](2-ethylhexyl)oxy]benzo[1,2-b:4,5-b']dithiophene-2,6-diyl][3-fluoro-2-[(2-ethylhexyl)carbonyl]thieno [3,4-b]thiophenediyl]] (PTB7):[6,6]-phenyl-C₇₁-butyric acid methyl ester (PC71BM) organic solar cells (OSCs) were investigated by optical simulation of a transfer matrix model (TMM), photo-induced charge extraction by linearly increasing voltage (photo-CELIV) technique, atomic force microscope (AFM), and the Onsager-Braun model analysis. BTA2 is an A2-A1-D-A1-A2-type nonfullerene small molecule with thiazolidine-2,4-dione, BTA, and indacenodithiophene as the terminal acceptor (A_2) , bridge acceptor (A_1) , and central donor (D), respectively. The short-circuit current density of the OSCs with BTA2 can be enhanced significantly owing to a complementary absorption spectrum. The optical simulation of TMM shows that the ternary OSCs exhibit higher internal absorption than the traditional binary OSCs without BTA2, resulting in more photogenerated excitons in the ternary OSCs. The photo-CELIV investigation indicates that the ternary OSCs suffer higher charge traplimited bimolecular recombination than the binary OSCs. AFM images show that BTA2 aggravates the phase separation between the donor and the acceptor, which is disadvantageous to charge carrier transport. The Onsager-Braun model analysis confirms that despite the charge

E-mail: wjtian@jlu.edu.cn

collection efficiency of the ternary OSCs being lower than that of the binary OSCs, the optimized photon absorption and exciton generation processes of the ternary OSCs achieve an increase in photogenerated current and thus improve power conversion efficiency.

Keywords third component, organic solar cells, charge carrier generation, charge carrier recombination, bimolecular recombination

1 Introduction

Organic solar cells (OSCs) have attracted significant interest in recent decades owing to their simple device structure, easy processing, low-cost fabrication, light weight, and flexibility [1–5]. By designing new OSC materials and device structures, the performance of OSCs has significantly improved [6–11]. Currently, the optimal power conversion efficiency (PCE) of OSCs is more than 11% [12–16]; moreover, the PCE of non-fullerene OSCs has reached more than 18% [17]. The PCE of the tandem OSCs is 17.3% or more [18]. However, for the future commercialization of organic photovoltaics, further improvement in PCE is required; moreover, enhancing the short-circuit current density (J_{sc}) of the OSCs is a useful method to improve PCE [19].

Researchers have designed and synthesized many series of low-bandgap photovoltaic molecules, including polymer donor materials and small molecule acceptor materials, to enhance the absorption of OSCs, and thus improve the J_{sc} [20–23]. However, because of the inherent

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absorption property of the organic materials, it is still challenging to completely include the solar spectrum by merely using a donor material and an acceptor material. Conversely, organic materials generally have low charge carrier mobility. To obtain optimal charge collection, the active layer of the OSCs usually must be significantly thin (as thin as 100 nm), which makes it impossible to completely capture all the incident sunlight within its absorption range; further, this also limits the improvement of J_{sc} [24]. The tandem OSCs that include more than one active layer with complementary absorption spectrum can avoid the problem of narrow spectral response range in single-layer devices; moreover, they can utilize the solar spectrum more effectively, thereby improving the efficiency of photovoltaic devices [25-27]. Nevertheless, the preparation of tandem OSCs is considerably complex, and it is expensive to fabricate these kinds of devices, which limits their future mass production. In contrast, the strategy of designing ternary OSCs can not only optimize the absorption of the OSCs, but also help to maintain the simplicity of device preparation. The ternary OSCs can significantly improve the J_{sc} and device performance. However, although over the last couple of years considerable work has been performed to improve the PCE of OSCs by fabricating ternary devices, there are relatively few studies on the mechanism of introduction of the third component and its effect on the overall photoelectric process of the device; particularly, considerably few studies have analyzed the effects of the third component on the conversion of solar photons to electrons and the charge carrier behavior of the OSCs [8,17,28].

In recent years, benzotriazole (BTA)-based A2-A1-D-A₁-A₂-type non-fullerene small molecular acceptors were developed with high-lying and tunable lowest unoccupied molecular orbital energy levels (between -3.38 eV and -3.61 eV), which guarantees the OSCs based on these molecules with significantly high open circuit voltage (V_{oc}) of 1.02 V to 1.24 V [29-31]. In this work, BTA2, as the third component, was introduced to the OSCs based on poly[[4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-b:4,5-b']dithiophene-2,6-diyl][3-fluoro-2-[(2-ethylhexyl)carbonyl]thieno [3,4-b]thiophenediyl]] (PTB7):[6,6]-phenyl-C₇₁-butyric acid methyl ester (PC₇₁BM). The J_{sc} of the ternary OSCs with BTA2 was obviously increased when compared to that of the binary OSCs without BTA2, leading to an improved device PCE. The analysis of the optical simulation by using the transfer matrix model (TMM) indicated that the ternary OSCs obtained complementary internal absorption spectra when compared to the OSCs without BTA2, which resulted in more photogenerated excitons in ternary OSCs. The photo-induced charge extraction by linearly increasing voltage (photo-CELIV) technique was utilized to investigate the effect of BTA2 on the charge carrier behavior of the solar cells, and it indicated that the ternary OSCs suffered more serious traplimited bimolecular recombination after exciton dissociation and free charge carrier generation. The Onsager– Braun model was applied to analyze the loss of the photogenerated current between the ternary OSCs and the binary OSCs. It indicated that even though the charge collection efficiency of the ternary OSCs was lower, the photogenerated current can be improved because of the optimized absorption property of the photon and exciton generation process owing to introduction of BTA2, which ensured the improvement of J_{sc} and PCE of the ternary OSCs.

2 Experimental

2.1 Materials

PTB7 was bought from 1-Material Chemscitech Inc. (Canada). PC₇₁BM was bought from American Dye Source Inc. (USA). Both PTB7 and PC₇₁BM were used without further treatments. The detailed synthesis and properties of the third component, BTA2, can be obtained from our previous report [30]. Acetone (analytical reagent) was purchased from Beijing Chemical Reagents Company. Isopropanol (analytical reagent) was obtained from Tianjin Tiantai Fine Chemicals Co., Ltd. Chlorobenzene (chromatographically pure) was obtained from Aldrich (USA). Poly(3,4-ethylene dioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) was bought from H.C. Starck (Baytron PVP AI4083). All the reagents and solvents were used without further purification.

2.2 Photovoltaic device fabrication and characterization

The utilized structure for the bulk heterojunction photovoltaic devices was indium tin oxide (ITO)/PEDOT:PSS/ PTB7:PC71BM with or without BTA2/LiF:Al. The detailed processes for cleaning the ITO-covered glass substrates and preparing the PEDOT:PSS layers were reported in our previous work [32]. The mixed solutions for the active layers of the OSCs were prepared as follows: PTB7 and PC71BM (1:1.5, w/w) were dissolved in chlorobenzene, and the total solution concentration was 25 mg·mL⁻¹. Then, the third component, BTA2, was added into this solution with 0%, 5%, 8%, 10%, 15%, and 20% mass concentrations. Moreover, a 3% volume concentration of solvent additive, i.e., 1,8-diiodoctane (DIO), was also added to these solutions to prepare different solutions for the active layers. Under the protection of nitrogen in the glove box, the active layers were prepared by spin-coating the mixed solutions onto the PEDOT:PSS layer, and films with a thickness of approximately 100 nm, which was measured using a Veeco Dektak 150 Surface Profilometer, were obtained by adjusting the spin speed and time. The residue DIO was removed by placing the active layers in a vacuum environment overnight (8 to 12 h). Finally, a cathode of approximately 1 nm of LiF and approximately 100 nm of Al was thermally evaporated under a pressure of 5×10^{-4} Pa. The size of every solar cell was 2 mm × 2 mm. The characterization methods and instruments for measuring the current density-voltage (*J-V*) characteristics, incident photon-to-current efficiency (IPCE) spectra, and photo-CELIV experiments were the same as that utilized in our previous reports [32,33].

2.3 Thin film characterization

A Veeco Dektak 150 Surface Profilometer was utilized to perform the thickness measurements for the films of PEDOT:PSS, PTB7:PC₇₁BM with or without BTA2, and LiF/Al. An atomic force microscope (AFM) morphology was scanned using the Dimension FastScan from BRU-KER. The ultraviolet–visible absorption spectra were measured using a Shimadzu UV-3600 spectrophotometer.

The Horiba Jobin Yvon UVISEL 2 ellipsometer was used to perform the ellipsometry experiments. A clean Si wafer was used as the substrate and PEDOT:PSS solution was spin-coated onto the Si substrate. Then, the mixed solutions containing two components and three components were individually spin-coated onto the substrate of Si/PEDOT:PSS to prepare the binary and ternary active layers, respectively. All the measurements were performed at room temperature [33].

3 Results and discussion

3.1 Performance of organic solar cell

The molecular structures of BTA2, PTB7, and PC71BM and the energy band diagram of the molecules in the devices are displayed in Fig. 1. In BTA2, the groups of thiazolidine-2,4-dione, BTA, and indacenodithiophene serve as the terminal acceptor (A_2) , bridge acceptor (A_1) , and central donor (D), respectively. The absorption spectra of PTB7, BTA2, and PC₇₁BM, which were in the form of films prepared by the spin-coating of their respective chlorobenzene solutions, and the standard spectral irradiance (air mass 1.5 (AM1.5)) are exhibited in Fig. 2. The primary absorption region of the electron donor material, i.e., PTB7, in the traditional binary solar cells is observed to be between 350 and 500 nm and that of PC₇₁BM is between 600 and 750 nm. The AM1.5 shows that the radiation energy of sunlight is high, in the range of 450 to 650 nm. Obviously, the traditional binary OSCs could not fully absorb and utilize the energy of sunlight. To fully utilize the sunlight energy, the third component BTA2 was introduced into the binary OSCs. From Fig. 2, it can be determined that the primary light absorption range of BTA2 is between 450 and 650 nm, which can effectively complement the absorption spectrum of a binary PTB7: $PC_{71}BM$ blend film.

The concentration of BTA2 in the ternary OSCs was optimized. Figure 3(a) shows the J-V curves of the OSCs containing varying mass concentrations of BTA2 under the radiation of AM1.5. We can observe that the J-V curves of the OSCs change significantly according to the concentration of BTA2 varying from 5% to 20%. Moreover, it can be noted that the solar cell with 10% mass concentration of BTA2 has the optimal J-V characteristics and device performance. Figure 3(b) exhibits the contrast between the J-V curves of the traditional binary OSCs without BTA2 and the optimized ternary OSCs with 10% mass concentration of BTA2. The device parameters for the two solar cells illustrated in Fig. 3(b) are listed in Table 1. In contrast to the binary OSCs, the introduction of 10% mass concentration of BTA2 improved the J_{sc} of the device from 15.3 to 16.7 mA \cdot cm⁻²; moreover, the V_{oc} has a slight improvement from 0.73 to 0.74 V, while the fill factor decreased marginally, which resulted in an increase in the PCE of the device from 7.2% to 8.0%.

3.2 Optical analysis and simulation

Figure 4(a) shows the IPCE spectra of the traditional PTB7:PC71BM binary OSCs and optimized ternary OSCs with 10% mass concentration of BTA2. It can be observed that the IPCE spectrum of the binary OSCs contains a concave trend between 450 and 650 nm. However, as to the ternary OSCs with 10% mass concentration of BTA2, it exhibits a wide peak in the same wavelength range. Obviously, the IPCE of the ternary OSCs with 10% mass concentration of BTA2 is higher than that of the binary OSCs without BTA2 in the wavelength range between 450 and 650 nm. This suggests that the introduction of BTA2 improved the external quantum efficiency (EQE) of the devices. The changing trend of IPCE spectra of the devices matches that of the absorption spectra (Fig. 4(b)). The PTB7:PC71BM active layer with 10% mass concentration of BTA2 demonstrated higher absorption characteristics in the wavelength between 450 and 650 nm. This indicates that the introduction of BTA2 to the PTB7:PC71BM blend film improves the utilization of photon to electron conversion in the 450 to 650 nm wavelength range through complementary optical absorption.

Internal absorption (Q) is the number of incident photons absorbed by the active layer of the OSCs [33]; further, internal quantum efficiency (IQE) is determined as the number of extracted electrons converted from the current divided by the absorbed photon number in an active layer [34]. Thus, detailed information about the absorbed light contributing to the photocurrent can be obtained from IQE [33].To study the influence of the third component, BTA2, on the optical property of the ternary OSCs, the TMM was used to calculate the values of Q and IQE of the binary and ternary OSCs. The refractive index





Fig. 1 (a) Molecular structures of the third component (BTA2), PTB7, and PC₇₁BM; (b) energy band diagram to represent the energy levels.



Fig. 2 Spectral irradiance of the air mass 1.5 under different wavelengths and the absorption spectra of PTB7, $PC_{71}BM$, and the third component, i.e., BTA2, in films prepared by spin-coating of the corresponding chlorobenzene solutions.



Fig. 3 (a) J-V characteristics of PTB7:PC₇₁BM OSCs with different mass concentration of BTA2; (b) J-V characteristics of the optimized ternary OSCs and the traditional binary OSCs without BTA2.

 Table 1
 Device performance of the traditional binary OSCs and the optimized ternary OSCs with 10% mass concentration of BTA2

| Devices | $V_{\rm oc}/{ m V}$ | $J_{\rm sc}/({\rm mA}\cdot{\rm cm}^{-2})$ | FF/% | $\mu_{\rm e}/({\rm cm}^2\cdot {\rm V}^{-1}\cdot {\rm s}^{-1})$ | $\mu_{\rm h}/({\rm cm}^2\cdot{\rm V}^{-1}\cdot{\rm s}^{-1})$ | PCE/% |
|---------------|---------------------|---|-------|--|--|-------|
| Without BTA2 | 0.73 | 15.3 | 65.25 | 4.35×10^{-4} | 1.83×10^{-4} | 7.2 |
| With 10% BTA2 | 0.74 | 16.7 | 64.14 | 2.63×10^{-4} | 9.8×10^{-5} | 8.0 |



Fig. 4 Comparitive analysis between the optimized ternary OSCs with 10% mass concentration of BTA2 and the traditional binary OSCs without BTA2 corresponding to (a) incident photon-to-current efficiency spectra and (b) absorption spectra.

and extinction coefficient of each layer material in different wavelength ranges were obtained by ellipsometry [33]. Then, the Q of the active layer at different wavelengths was calculated using TMM. IQE was calculated using the formula, i.e., IQE = EQE/Q.

Figure 5 shows the Q and IQE values of the binary and ternary OSCs. From Fig. 5(c), it can be observed that the introduction of the third component, BTA2, improves Q of the active layer under light condition; thus, it increases the number of photons absorbed by the OSCs. The enhanced Q in the active layer is primarily concentrated in the 450 to 650 nm wavelength range, indicating that it is the result of the complementary spectral absorption of BTA2 to the active layer of PTB7:PC₇₁BM. Owing to the high radiation

energy of the standard solar spectrum in the 450 to 650 nm wavelength range, the increase of Q in this wavelength range implies that more photo-induced excitons will be generated in the devices with the introduction of the third component, which significantly improves the charge carrier generation. Figure 5(d) shows the IQE in the binary and ternary OSCs. The IQE of the device is primarily determined in correlation with the charge carrier transport and recombination process after the exciton generation in the OSCs. As the IQE of the two devices at different wavelengths exhibited high and low values, the influence of the third component on charge carrier recombination could not be directly obtained based on the IQE.



Fig. 5 Q, EQE, and IQE spectra of (a) the traditional binary OSCs without BTA2 and (b) the optimized ternary OSCs with 10% mass concentration of BTA2; (c) Q and (d) IQE calculated and analyzed by the transfer matrix optical model.

3.3 Charge carrier recombination

In the process of carrier transport, the carriers with opposite charges produced by different charge transfer state excitons may meet and recombine, which is called non-geminate recombination [35,36]. In bulk heterojunction OSCs, non-geminate recombination primarily includes trap-free bimolecular recombination and traplimited (also called as trap-assisted) bimolecular recombination; moreover, the latter is the dominant recombination [37]. The trap-limited bimolecular recombination can be studied by using the photo-CELIV technique [37]. To further study the influence of the third component on the charge recombination in the ternary OSCs, the charge decay behavior with delay time for the binary and ternary OSCs was investigated using photo-CELIV technique. Figures 6(a) and 6(b) show the photo-CELIV transients recorded at different delay times (20 to 2000 µs) for the binary and ternary OSCs, respectively. The intensity of the photo-CELIV transients decreased progressively with the increase in delay time, which resulted from the charge carrier recombination. After integrating the photo-CELIV transients over delay time, we obtained the time-dependent charge carrier density (Fig. 6(c)). Based on the recombination model of Mozer et al. [38], the experimental curves in Fig. 6(c) can be fit through mathematical calculation. In the

dispersive regime of the active layer, assuming that the film is electrically neutral, the relationship between charge carrier density n(t) and time is as shown below [32,37]:

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$$u(t) = \frac{n_0}{1 + (t/\tau)^{\alpha}},$$
(1)

where, n_0 represents the initial charge carrier density and *t* corresponds to the delay time. τ represents the recombination lifetime and α ($0 < \alpha < 1$) corresponds to the dispersion parameter.

In the disordered active layer, while considering the electric neutral condition, the relationship between bimolecular recombination rate γ_{bi} and n(t) is calculated according to the following equation [32,37]

$$y_{\rm bi}(t) = -\frac{\mathrm{d}n(t)/\mathrm{d}t}{n^2(t)}.$$
(2)

Substituting Eq. (1) into Eq. (2), γ_{bi} can be calculated as follows [32,37]:

$$\gamma_{\rm bi}(t) = \alpha \tau^{-1} n_0^{-1} (t \tau^{-1})^{\alpha - 1}.$$
 (3)

The solid lines in Fig. 6(c) are the curves obtained by fitting. Obviously, the fitting results are well consistent with the experiment data. Furthermore, it can be observed that the charge carrier density of the two OSCs decreases



Fig. 6 Transients of photo-induced charge extraction by linearly increasing voltage technique versus delay time of PTB7:PC₇₁BM solar cells (a) without the third component BTA2 and (b) with 10% BTA2; (c) Time-dependent charge carrier density of PTB7:PC₇₁BM solar cells with and without the third component of 10% BTA2; here, the solid line is the fitting curve; (d) Trap-limited bimolecular recombination rate versus delay time of PTB7:PC₇₁BM solar cells with and without the third component of 10% BTA2; here, the solid line is the fitting curve; (d) Trap-limited bimolecular recombination rate versus delay time of PTB7:PC₇₁BM solar cells with and without the third component of 10% BTA2.

with the increase in delay time, which is due to the charge carrier recombination. The parameters n_0 , τ , and α for the OSCs can be obtained through fitting and they are listed in Table 2. It can be noted that in contrast to the OSCs without BTA2, the introduction of BTA2 into the OSCs resulted in the n_0 of the ternary OSCs increasing from 8.22×10^{16} to 9.34×10^{16} cm⁻³. However, as the delay time lengthened, the charge carrier density in the ternary OSCs declined faster than that in the binary OSCs. This implies that after the free charge carrier generation, the introduction of the third component will result in more charge carriers loss in the processes of charge carrier transport and extraction in the ternary OSCs. The dispersion parameter α of the binary and ternary OSCs was 0.897 and 0.821, respectively, indicating that the recombination belongs to trap-limited bimolecular recombination with regard to the two OSCs (when α is equal to 1, the recombination mechanism is trap-free bimolecular recombination and when α is less than 1, the recombination mechanism is trap-limited bimolecular recombination [39]). The charge carrier

bimolecular recombination rate γ_{bi} can be calculated according to formula (3), as shown in Fig. 6(d). We can observe that the plots for the binary and ternary OSCs demonstrate a marginal decrease with the increase in delay time. However, the γ_{bi} of the binary OSCs (5.94×10⁻¹³ cm³·s⁻¹) is significantly lower than that of the ternary OSCs (9.18×10^{-13} cm³·s⁻¹), resulting in the recombination lifetime τ increasing from 7.79 µs for the ternary OSCs to 9.14 µs for the binary OSCs (Table 2). The results imply that in contrast to the binary OSCs, the charge carriers corresponding to the ternary OSCs are more likely to be trapped and bimolecular recombination occurs after the charge carrier generation. Although the initial charge carrier density of the ternary OSCs excited by laser is higher, the carrier lifetime is shorter and decay is faster in the process of transport and extraction. Therefore, the introduction of 10% mass concentration of the third component, BTA2, into the PTB7:PC71BM solar cell is disadvantageous to the transport and extraction after the generation of carriers.

 Table 2
 Parameters of the OSCs with and without the third component of 10% BTA2 from the fitting in Fig. 6(c)

| Devices | $n_0/{\rm cm}^{-3}$ | $\tau/\mu s$ | α | $\gamma_{\rm bi}/({\rm cm}^3\cdot{\rm s}^{-1})$ |
|---------------|-----------------------|--------------|-------|---|
| Without BTA2 | 8.22×10^{16} | 9.14 | 0.897 | $5.94 \times 10^{-13} \\ 9.18 \times 10^{-13}$ |
| With 10% BTA2 | 9.34×10^{16} | 7.79 | 0.821 | |

3.4 Morphology of the active layer

Figure 7 displays AFM images of the active layers of the binary and ternary OSCs. The AFM images demonstrate similar root-mean-square (RMS) values of surface roughness for the topography images. The RMS of the binary OSCs is 1.3 nm, and that of the ternary OSCs is 1.4 nm. However, their phase images are significantly different. When compared to the active layer without BTA2, the active layer with 10% mass concentration of BTA2 demonstrated a more severe degree of phase separation and a larger phase-domain scale. It indicates that the third component, BTA2, has a poor compatibility with the PTB7 and PCBM, which increases the phase separation of the blends; moreover, the optimal cross-linked blending networks of the donor and acceptor are damaged with the introduction of the BTA2. The increased phase separation and damaged blending networks are not conducive to charge transport.

Figure 8 shows the space-charge-limited current investigation results for the electron-only and hole-only devices with and without the third component of 10% BTA2. The structure for the former device is glass/ZnO/PTB7: PC₇₁BM with or without 10% BTA2/LiF/Al, and that for the latter device is glass/PEDOT:PSS/PTB7:PC₇₁BM with or without 10% BTA2/Pd. Their electron and hole motilities are listed in Table 1. It shows that the ternary OSC has lower electron and hole motilities when compared to the binary OSC (Their electron motilities were 2.63×10^{-4} and 4.35×10^{-4} cm² · V⁻¹ · s⁻¹, respectively, and the hole motilities were 9.8×10^{-5} and 1.83×10^{-4} cm² · V⁻¹ · s⁻¹, respectively.). The results indicate that the introduction of the third component, BTA2, is disadvantageous to charge transport as it decreases the electron and hole mobilities of the OSCs.

3.5 Loss of the photogenerated current

To further explore the influence of BTA2 on the charge collection efficiency under operation conditions, the relationship between photocurrent density $(J_{\rm ph})$ and effective voltage $(V_{\rm eff})$ of the binary and ternary OSCs was investigated (Fig. 9), from which the charge collection efficiency $\eta_{\rm cc}$ under operation conditions was estimated. $J_{\rm ph}$ and $V_{\rm eff}$ are defined according to the following two equations,

$$J_{\rm ph} = J_{\rm illumination} - J_{\rm dark},\tag{4}$$

$$V_{\rm eff} = V_0 - V_{\rm app}.$$
 (5)

Here, $J_{\text{illumination}}$ and J_{dark} correspond to the current densities under illumination and in the dark, respectively. V_0 represents the voltage at the condition of the minimum



Fig. 7 Atomic force microscope phase (a1 and b1) and topography (a2 and b2) images of the active layer of PTB7:PC₇₁BM with (a1) (a2) and without (b1) (b2) the third component of 10% BTA2.



Fig. 8 Space-charge-limited current measurements for the (a) electron-only and (b) hole-only devices with and without the third component of 10% BTA2.



Fig. 9 Experimental and fitted effective photocurrent density $(J_{\text{ph}} = J_{\text{illumination}} - J_{\text{dark}})$ versus the effective applied voltage $(V - V_0)$ in the OSCs with the third component of 10% BTA2 and without BTA2.

Table 3 Parameters of the OSCs with the third component of 10%BTA2 and without BTA2 from the fitting with the Onsager–Braun model

| Devices | $\gamma_{\rm bi}/({\rm cm}^3\cdot{\rm s}^{-1})$ | $G/(\times 10^{25} \text{ m}^{-3})$ | $\eta_{ m cc}$ |
|---------------|---|-------------------------------------|----------------|
| With 10% BTA2 | 9.18×10^{-13} | 1.25 | 85% |
| Without BTA2 | 5.94×10^{-13} | 1.03 | 91% |

photocurrent ($J_{\text{illumination}} = J_{\text{dark}}$), and V_{app} is the applied bias. When V_{eff} ranges from the short-circuit point to the maximum power point, the J_{ph} - V_{eff} curves are limited by the monomolecular recombination. However, with the V_{eff} increasing continuously, ranging between the maximum power point and the open-circuit voltage point, the J_{ph} - V_{eff} curves are predominantly limited by the bimolecular recombination [33,40]. When V_{eff} is sufficiently large, almost all the photogenerated charges will be collected by the respective electrodes. However, when V_{eff} is low, the charge recombination increases, resulting in a partial loss of photogenerated charges. Under the specific V_{eff} condition, η_{cc} can be calculated according to the following formula:

$$\eta_{\rm cc}(I, V_{\rm eff}) = \frac{J_{\rm ph}(I, V_{\rm eff})}{J_{\rm ph,sat}(I)}.$$
(6)

The Onsager-Braun model was used to numerically fit the net effective photocurrent. Then, we obtained the total number of photogenerated excitons (G) and charge collection efficiency η_{cc} of the binary and ternary OSCs. The solid lines in Fig. 9 indicate the curves obtained by fitting. It can be observed that the fitting results match well with the experiment results. The parameters from the fitting results are listed in Table 3. It can be observed that the G of the ternary OSCs $(1.25 \times 10^{25} \text{ m}^{-3})$ is higher than that of the binary OSCs $(1.03 \times 10^{25} \text{ m}^{-3})$ under AM1.5 sunlight. The results indicate that owing to the introduction of BTA2, the active layer can absorb and utilize the sunlight more efficiently, which increases the number of excitons generated by the light. However, it should be noted that the introduction of BTA2 is unprofitable for charge transport and extraction, resulting in more severe charge carrier recombination and greater losses of charge carriers. This results in a lower charge collection efficiency for ternary devices under short-circuit conditions (85% for ternary devices and 91% for binary devices). Nevertheless, owing to the increase in G, the short-circuit current of the ternary OSCs is still greater than that of the binary OSCs.

4 Conclusions

In conclusion, the influence of the small molecular BTA2 as the third component on the photon absorption and exciton generation processes, charge carrier transport, and extraction process of PTB7:PC₇₁BM photovoltaic system was investigated. The results show that J_{sc} of the ternary OSCs was increased significantly and the PCE was optimized owing to the addition of 10% mass concentration of BTA2. The optical simulation based on the TMM demonstrated that the ternary OSCs with BTA2 obtained complementary internal absorption in the 450 to 650 nm wavelength range, which resulted in more photogenerated

excitons in the ternary OSCs in contrast to that of the traditional binary OSCs without BTA2. The photo-CELIV investigation results confirmed that the ternary OSCs suffered more serious trap-limited bimolecular recombination during the charge carrier transport and extraction processes than the binary OSCs. Moreover, the active layer of the ternary OSCs demonstrated more severe phase separation, which was not conducive to the transport of the charge carrier. The results of the photogenerated current loss by Onsager–Braun model showed that although the charge collection efficiency in the ternary OSCs was lower, the photogenerated current was improved with the addition of BTA2 owing to the optimized photon absorption and exciton generation processes, which achieved improved J_{sc} and PCE for the ternary OSCs.

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