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Efficient Ternary Polymer Solar Cells with Parallel-linkage Structure

Miao Zhang, Fujun Zhang,* Jian Wang, Qiaoshi An, Qianqian Sun

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A series of ternary polymer solar cells (PSCs) were fabricated based on two narrow bandgap polymers PTB7 and PBDT-TS1 as donor and $PC_{71}BM$ as acceptor. The performances of ternary PSCs are monotonously increased along with the PBDT-TS1 doping ratios up to 80 wt% in donors. The champion power conversion efficiency (PCE) of ternary PSCs achieves 7.91% with an open circuit voltage (V_{oc}) of 0.76 V, a short circuit current density (J_{sc}) of 18.85 mA/cm² and a fill factor (FF) of 55.2% for the active layers with 80 wt% PBDT-TS1 doping ratio in donors. The optimized ternary PSCs show a 12.8% improvement compared with the champion PCE of 7.01% for the binary PSCs with PBDT-TS1 as donor and a 28.2% improvement compared with the champion PCE of 6.17% for the binary PSCs with PTB7 as donor. The FFs of all ternary PSCs are larger than 54%, indicating the efficient charge carrier transport channels in the ternary active layers. The energy or charge transfer between PTB7 and PBDT-TS1 should be neglected according to the investigation on photoluminescence spectra of blend films and the current density-voltage (J-V) curves of devices without acceptor in the active layers. The ternary PSCs should be parallel-linkage structure with donors independently working with acceptor, which may be the most promising strategy for obtaining highly efficient ternary PSCs.

Introduction

Bulk heterojunction polymer solar cells (PSCs) have been envisioned as one of the promising candidate energy converting devices with the advantage of light weight, low-cost, flexibility, environmental friendship and ease of large-area processing.¹⁻³ Many efficient methods have been carried out to improve the performance of PSCs, such as synthesis of new materials with narrow bandgap,^{4, 5,} ⁶ optimization of morphology and phase separation,^{7, 8} adoption of interfacial buffer layer 9, 10 and development of new device architectures.^{11, 12} The champion power conversion efficiency (PCE) achieves about 10% or 11% for bulk heterojunction or tandem solar cells, respectively.^{13, 14} It is known that the performance of PSCs is mainly limited by insufficient photon harvesting of the active layers due to the relatively narrow absorption spectral range (~100 nm) of organic/polymer materials.¹⁵ Tandem solar cells with multi-layers structure were designed to improve photon harvesting by employing two or more materials with complementary absorption spectra to harvest high and low energy photons, separately.¹⁶ However, the complicated multi-layers structure has serious technical challenges for its potential application of tandem solar cells, such as the processing of a robust intermediated layer, the optimization thickness of the sub-active layers. The intermediated layer between top and bottom sub-cells is one of the most important features to obtain high performance tandem solar cells, which should have rather low resistance and high transmittance. The thickness of sub-

Key Laboratory of Luminescence and Optical Information, Ministry of Education, Beijing Jiaotong University, Beijing 100044, China Corresponding Author: fizhang@bitu.edu.cn (Fujun) active layers is also one of the key parameters to better balance short circuit current density (J_{SC}) of the top and bottom sub-cells. An elegant alternative strategy is incorporating the third component into binary blend films to prepare ternary PSCs for the performance improvement.^{17, 18} Ternary PSCs maintain the simplicity of the processing conditions used for single-junction PSCs and strong photon harvesting ability by employing two materials with complementary absorption spectra.^{19, 20} Recently, the PCE of ternary PSCs has approached or even exceeded 10%, which indicates that ternary strategy may be an effective and simple method to improve the performance of PSCs.^{21, 22}

Ternary PSCs can be classified as three categories including "two donors/one acceptor", "one donor/two acceptors" or "donor/nonvolatile additive/acceptor".23-25 For the ternary PSCs with two acceptors, the PCE of ternary PSCs can be optimized by adjusting the doping ratios of henyl-C71-butyric acid methyl ester (PC₇₁BM) or indene-C61 bisadduct (ICBA) in the acceptors.²⁶ The ternary PSCs exhibit a relatively large open circuit voltage (V_{OC}) for the high ICBA doping ratios in acceptors. A relatively large J_{SC} can be obtained for the ternary PSCs with high PC71BM doping ratios in acceptors. Zhan reported the high PCE of 8.24% ternary PSCs based on ICBA as electron-cascade acceptor in thieno[3,4b]thiophene/benzodithiophene (PTB7) and PC71BM blend system.²⁷ The second acceptor ICBA plays a bridging role between PTB7 and PC71BM for providing the more charge transfer or exciton dissociation routes. For the ternary PSCs with two donors, the complementary absorption spectra between two donors is the first key selection criteria to improve photon harvesting of the ternary active layers.²⁸ Another key selection criterion is similar the highest occupied molecular orbits (HOMO) levels of two donors for the

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better hole transport in the ternary active layers. For the early research on ternary PSCs with two donors, the main strategy is doping a narrow bandgap material into poly(3-hexylthiophene-2,5diyl) (P3HT) with PC₇₁BM or ICBA blend system.^{29, 30} The PCE of ternary PSCs can be improved about 20-30% compared with the optimized PCE of the corresponding binary PSCs. In fact, the PCE values of this kind of ternary PSCs are still less than 6% due to the relatively low PCE of the binary PSCs with P3HT as donor.³¹ Recently, a series of highly efficient ternary PSCs have been reported based on two narrow bandgap materials as donors. Yan et al. reported that the champion PCE of 8.33% for the ternary PSCs obtained when narrow bandgap material alkyldiketopyrrolopyrrole and dithienylthieno[3,2-b]thiophene (DPP-DTT) was doped in PTB7 and PC71BM blend system with 1 wt% in donors.32 Yu et al. reported that wide bandgap material poly-3-oxothieno[3,4-d]isothiazole-1,1dioxide/benzodithiophene (PID2) was doped into poly[4,8-bis(5-(2ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b'] dithiophene-co-3fluorothieno[3,4-b]thiophene-2-carboxylate] (PTB7-Th) and PC71BM blend system, the champion PCE of 9.2% was obtained for ternary PSCs with 20 wt% PID2 doping ratio in donors. The enhanced PCE was attributed to the energy transfer from PID2 to PTB7-Th and the increased photon harvesting by PID2 molecules.³³ For the most of ternary PSCs, the champion PCE has been obtained when the third component doping ratios are less than 20 wt% in donors or acceptors. The PCE of ternary PSCs will be substantially decreased when the third component doping ratios are larger than 20 wt% in donors, which is mainly due to the large phase separation resulting in the disrupted bicontinuous interpenetrated network in the ternary active layers.34 Therefore, photon harvesting ability of the third component cann't be efficiently utilized due to its limited doping weight in the ternary active layers. Recently, You et al. successfully reported parallel-linkage ternary PSCs, the champion PCE of 7.02% was obtained for the ternary PSCs with the two donors poly(benzodithiophene-dithienylthiadiazolopyridine) (DTPyT) and poly-(benzodithiophenedithienyldifluorobenzothiadiazole) (DTffBT) with the equal content (1:1, w/w) in the active layers.³⁵ The fill factors (FFs) of all ternary PSCs are kept more than 56% due to the efficient charge carrier transport in the ternary active layers. This means that two donors can independently work with the electron acceptor in the parallel-linkage ternary PSCs, which is mainly attributed to the similar chemical structure of the two donors preventing the apparent phase separation or disrupted bicontinuous interpenetrating network. It is believed that excitons generated in two donors can migrate to their respective donor/acceptor interface and then dissociate into free charge carriers in the parallel-linkage ternary PSCs. Up to now, few research on parallel-linkage ternary PSCs have been reported.³⁶ The underlying mechanism of parallel-linkage ternary PSCs is needed to be further investigated for improving the performance of ternary PSCs.

Recently, a series of narrow bandgap materials based on benzo[1,2-b:4,5-b']dithiophene (BDT) unit have been reported as efficient electron donors in PSCs. Among them, 2,6-bis(trimethylstannyl)-4,8-bis(5-(octylthio)-thiophen-2-yl)benzo[1,2-b:4,5-b']-dithiophene (PBDT-TS1) and PTB7 are popular materials with different bandgap.^{37, 38} Based on their absorption spectral complementation, PTB7 and PBDT-TS1 were selected to fabricate efficient ternary PSCs with PC₇₁BM as acceptor. The PCEs of

ternary PSCs are monotonously increased along with PBDT-TS1 doping ratios up to 80 wt% in donors. The champion PCE of ternary PSCs achieves 7.91% along with a V_{OC} of 0.76 V, a J_{SC} of 18.85 mA/cm² and a FF of 55.2% based on the ternary active layers with 80 wt% PBDT-TS1 doping ratio in donors. According to the investigation on the absorption spectra, photoluminescence (PL) spectra of blend films and current density-voltage (*J-V*) curves of PTB7:PBDT-TS1 devices, the fabricated ternary PSCs should be parallel-linkage structure. The efficient bicontinuous interpenetrating network and appropriate phase separation in the ternary active layers may be well kept during adjusting PBDT-TS1 doping ratios in donors for the optimization of photon harvesting.

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Experimental section

The glass substrates coated indium tin oxide (ITO) with a sheet resistance of 15 Ω / square were pre-cleaned consecutively in the ultrasonic baths containing acetone, detergent, de-ionized, and ethanol. The cleaned ITO-coated glass substrates were dried by high pure nitrogen gas and then treated by UV-ozone for 10 minutes to improve the work function of ITO glass substrates. Subsequently, poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS, purchased from H.C. Starck co. Ltd.) solution was spin-coated on the ITO-coated glass substrates at 5000 rounds per minutes (rpm) for 40 s and baked at 120°C for 15 minutes in air condition. Then the glass substrates spin-coated PEDOT:PSS films were transferred to a high-purity nitrogen-filled glove box where all operations on it were carried out to fabricated PSCs. The polymer PTB7 and fullerene derivative PC71BM (purchased from Luminescence Technology Corp.) and the polymer PBDT-TS1 (purchased from Organtec Materials Inc.) were used without any treatments. The PTB7, PBDT-TS1 and PC71BM and were codissolved in blend solvents chlorobenzene (CB) and 1,2dichlorobenzene (DCB) with volume ratio 1:1. The overall concentration of solutions was kept constant at 25 mg/mL with donors/acceptor weight ratio as 1:1.5, only difference is PBDT-TS1 doping ratios in donors from 0 wt % to 100 wt %. The prepared blend solutions were discontinuously heated and stirred at 75°C for 12 hours before spin-coating. Then 3 vol% 1,8-diiodooctance (DIO) additive was added into blend solutions to form final blend solutions. The active layers were fabricated by spin-coating final blend solutions on the PEDOT:PSS films at 1200 rpm for 40s. The conjugated polyelectrolyte poly[(9,9-bis(3'-(N,N-dimethylamino)propyl)-2,7-fluorene)-alt-2,7-(9,9-dioctylfluorene)] (PFN) was dissolved in methanol with addition of 0.25 vol% acetic acid to prepare 0.2 mg/mL solution. A two-steps strategy was carried out for the better adjusting phase separation and controlling the thickness of PFN interfacial buffer layer.³⁹ The 100 nm Al was deposited on the PFN films with a shadow mask by thermal evaporation under 10^{-4} Pa condition, and the thickness was monitored by a quartz crystal microbalance. The effective area of the device is about 3.8 mm^2 , which is defined by the vertical overlap of ITO anode and Al cathode.

The *J-V* curves of the PSCs were measured in dark or under light illumination using a Keithley 4200 source meter in air condition. The used AM 1.5G irradiation was provided by an ABET Sun 2000





Fig. 1. (a) Schematic configuration of the fabricated PSCs; (b) chemical structures of used materials PBDT-TS1, PTB7 and $PC_{71}BM$.

solar simulator with light intensity of 100 mW/cm². The external quantum efficiency (EQE) spectra of the PSCs were measured by a Zolix Solar Cell Scan 100. The absorption spectra of films were obtained by a Shimadzu UV-3101PC spectrometer. The thickness of the active layers is about 100 nm, which was measured by a Ambios Technology XP-2 stylus Profiler. Photoluminescence (PL) spectra of films were measured by a HORIBA Fluorolog®-3 spectrofluorometer system. The schematic diagram of the device configuration, chemical structures of used materials PBDT-TS1, PTB7 and $PC_{71}BM$ are shown in **Fig. 1a** and **1b**.

RESULTS AND DISCUSSION

A series of ternary PSCs were fabricated with PBDT-TS1x:PTB7(1x):PC71BM as the active layers, the subscript x indicates the PBDT-TS1 doping weight ratio in donors. The J-V curves of PSCs with different PBDT-TS1 doping ratios in donors were measured under AM 1.5G illumination with light intensity of 100 mW/cm², as shown in Fig. 2a. For the binary PSCs with PTB7:PC71BM as the active layers, the champion PCE of 6.17% is obtained with a V_{OC} of 0.72 V, a J_{SC} of 15.29 mA/cm² and a FF of 56.0%. For the binary PSCs with PBDT-TS1:PC71BM as the active layers, the optimized PCE achieves 7.01% with a V_{OC} of 0.79 V, a J_{SC} of 17.50 mA/cm² and a FF of 50.7%. For the ternary PSCs, the V_{OC} and J_{SC} are monotonously increased along with the increase of PBDT-TS1 doping ratios in donors up to 80 wt%. This change of V_{OC} is different from that of ternary PSCs with charge transfer mechanism where the V_{OC} of blend films is decided by the difference between the highest HOMO energy level of donors and the lowest unoccupied molecular orbits (LUMO) energy level of acceptor. The champion PCE of ternary PSCs achieves 7.91% with a V_{OC} of 0.76 V, a J_{SC} of 18.85 mA/cm² and a FF of 55.2% for PTB7_{0.2}:PBDT-TS1_{0.8}:PC71BM as the active layers. The PCE improvement should mainly be attributed to the increase of J_{SC} due to the enhanced photon harvesting of the ternary active layers, which can be further demonstrated from the EQE spectra of PSCs. The EQE spectra of all PSCs were measured and are shown in Fig. 2b. The markedly enhanced EQE values and widen response ranges are simultaneously obtained along with the increase of PBDT-TS1 doping ratios in donors, especially in the longer wavelength range. The optimized EQE spectra of ternary PSCs are obtained based on the active layers with 80 wt% PBDT-

TS1 doping ratio in donors. According to the EQE spectra of all PSCs, the J_{SC} values can be calculated based on the equation:

$$J_{SC} = \int EQE(\lambda) N(\lambda)q \ d\lambda$$

Here, $N(\lambda) = I_0/h\nu$ is the incident photon flux, q is the elementary charge in Coulomb (C).⁴⁰ The calculated J_{SC} values of all PSCs are slightly lower than the values obtained from *J*-*V* curves with about 8% deviation due to the decay of cells without encapsulation. The



Fig. 2. (a) J-V curves of all PSCs with different PBDT-TS1 doping ratios in donors as the active layers under AM 1.5G illumination with light intensity of 100 mW/cm²; (b) EQE spectra of all PSCs with different PBDT-TS1 doping ratios in donors as the active layers. All measurements were carried out in air conditions.

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PBDT-TS1	Voc	J_{SC}	Cal. J _{SC}	FF	R _{sh}	$\frac{R_s}{(\Omega \text{ cm}^2)}$	PCE (%)	
(wt%)	(V)	(mA/cm ²)	(mA/cm ²)	(%)	$(\Omega \text{ cm}^2)$		best	average
0	0.72	15.29	14.49	56.0	211	8.0	6.17	6.08
20	0.73	16.06	15.19	58.4	218	7.3	6.85	6.75
40	0.73	17.21	15.93	56.7	226	6.3	7.13	7.06
60	0.76	17.87	17.00	54.7	246	5.4	7.43	7.36
80	0.76	18.85	17.67	55.2	300	4.9	7.91	7.88
100	0.79	17.50	17.08	50.7	170	10.0	7.01	6.97

Table 1. Key photovoltaic parameters of all PSCs with different PBDT-TS1 doping ratios in donors.

detailed photovoltaic parameters of all PSCs are listed in Table 1.

To further confirm the contribution of PBDT-TS1 on the photon harvesting of the active layers, the absorption spectra of neat PTB7, PBDT-TS1, PC71BM and the ternary blend films with different PBDT-TS1 doping ratios in donors were measured and are shown in Fig. 3a and 3b. According to the Fig. 3a, polymer PTB7 exhibits an apparent absorption peak at about 670 nm and a shoulder absorption peak at about 620 nm. The polymer PBDT-TS1 exhibits a strong absorption peak at about 720 nm and a shoulder absorption peak at about 650 nm. There is an apparent absorption spectral complementation between PTB7 and PBDT-TS1, which is beneficial to enhancing photon harvesting of ternary active layers. The electron acceptor PC71BM has a strong photon harvesting ability in UV and visible light range, which can replenish photon harvesting of the ternary active layers in the shorter wavelength range. As seen from the Fig. 3b, it is apparent that the absorption spectra of ternary blend films are widened along with the increase of PBDT-TS1 doping ratios in donors. Meanwhile, the absorption intensity of ternary blend films was enhanced in the shorter wavelength range along with the increase of PBDT-TS1 doping ratios in donors. The absorption spectra of ternary active layers can well explain the EQE spectral change of ternary PSCs along with the increase of PBDT-TS1 doping ratios in donors.

To further confirm the effect of PBDT-TS1 doping ratios in donors on the photon harvesting and charge carrier transport, the photocurrent density (J_{ph}) versus effective voltage (V_{eff}) curves of binary PSCs and the optimized ternary PSCs were investigated and are shown in **Fig. 4a**. Here, J_{ph} is defined as $J_{ph} = J_{l} - J_{d}$, where J_{l} and J_d are the current density under 100 mW/cm² illumination and in dark, respectively. The V_{eff} is defined as $V_{eff} = V_0 - V_a$, where V_0 is the voltage at the point of $J_{ph} = 0$ and V_a is the applied bias voltage.⁴¹ The J_{ph} values of all PSCs rapidly arrive to the saturation state at about $V_{eff} = 0.2$ V, indicating the efficient charge carrier transport channels formed in the binary and ternary active layers. Assuming the exciton dissociation efficiency and charge carrier collection efficiency are unity at $V_{eff} = 2$ V, the saturation current density (J_{sat}) is mainly determined by maximum exciton generation rate (G_{max}) . As a result, $J_{sat} = qLG_{max}$, where q is elementary charge and L is the thickness of the active layers.³³ The J_{sat} of optimized ternary PSCs is 21.79 mA/cm², which is much larger than that of 18.01 mA/cm² for the binary PSCs with PTB7 as donor and 20.36 mA/cm² for the

binary PSCs with PBDT-TS1 as donor. Therefore, the G_{max} values are 1.36×10^{-26} m⁻³s⁻¹ for the ternary PSCs with PTB7_{0.2}:PBDT-TS1_{0.8} as donors, 1.13×10^{-26} m⁻³s⁻¹ or 1.27×10^{-26} m⁻³s⁻¹ for the binary PSCs with PTB7 or PBDT-TS1 as donor. It means that the ternary PTB7_{0.2}:PBDT-TS1_{0.8} active layers can harvest the more photons in the whole spectral range. It is known that the exciton dissociation, charge carrier transport and collection efficiency can also be assessed by the J_{ph}/J_{sat} values under short circuit condition.⁹ The



Fig. 3. (a) Normalized absorption spectra of neat PBDT-TS1, PTB7 and $PC_{71}BM$ film; (b) absorption spectra of ternary PTB7:PBDT-TS1:PC₇₁BM blend films with different PBDT-TS1 doping ratios in donors.

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Fig. 4. (a) $J_{ph}-V_{eff}$ curves of PSCs with 0 wt%, 80 wt% and 100 wt% PBDT-TS1 doping ratios in donors; (b) PL spectra of neat PBDT-TS1, neat PTB7, and blend films under 690 nm light excitation; (c) J-V characteristic curves of PSCs without acceptor under AM 1.5G illumination; (d) schematic working mechanism of the ternary PSCs.

 J_{ph}/J_{sat} value is 84.8 % for the binary PSCs with PTB7 as donor, 86.5 % for the ternary PSCs with PTB7_{0.2}:PBDT-TS1_{0.8} as donors, and 85.1 % for the binary PSCs with PBDT-TS1 as donor under short circuit conditions, respectively. The efficient exciton dissociation can be confirmed from the PL spectra of neat PTB7 and PBDT-TS1 films as well as the binary or ternary blend films, as shown in the inserted image of Fig. 4a. The PL emission of PTB7 or PBDT-TS1 was markedly quenched by PC₇₁BM in the blend films. It means that efficient charge carrier transport and collect can be well kept in the ternary solar cells. To clarify the molecular interaction between PTB7 and PBDT-TS1, the PL spectra of blend films without PC71BM were measured and are shown in Fig. 4b. Both PL emission peak of PTB7 and PBDT-TS1 are about 780 nm due to their similar bandgap of 1.8 eV. It is highlighted that PL emission intensity of PBDT-TS1 films is stronger than that of PTB7 films under the same excitation conditions. The emission intensity of blend films was almost linearly increased along with the increase of PBDT-TS1 doping ratios. It means that the energy transfer between PTB7 and PBDT-TS1 can be neglected according to the PL emission intensity of blend films.

To further exclude the charge transfer between PTB7 and PBDT-TS1, three kinds of devices ITO/PEDOT:PSS/active layers/Al were fabricated with the neat PTB7, PBDT-TS1 or blend PTB7:PBDT-TS1(1:1, w/w) as the active layers, respectively. The J-V curves of

devices were measured under AM 1.5G illumination with light intensity of 100 mW/cm² and are shown in **Fig. 4c**. As we can envisage, the J_{SC} of all devices are rather low due to the absence of PC₇₁BM in the active layers under light illumination. The J_{SC} of devices with PTB7:PBDT-TS1 as the active layer is in the between that of device with PTB7 or PBDT-TS1 as the active layers, suggesting an inefficient exciton dissociation or charge transfer between PTB7 and PBDT-TS1 interfaces. According to the above analysis, the schematic working mechanism diagram of ternary PSCs is described as the **Fig. 4d**. The two donors PTB7 and PBDT-TS1 can independently work with PC₇₁BM as sub-cells, the ternary PSCs can be considered as the parallel-linkage structure.

It is known that charge carrier transport in the active layers also plays the key role in determining the performance of PSCs, especially for the balance of hole and electron transport in the active layers. The hole-only devices with the structure of ITO/PEDOT:PSS/active layer (100 nm)/MoO₃/Ag and electron-only devices with the structure of Al/active layer (100 nm)/Al were prepared to characterize the effect of PBDT-TS1 doping ratios in donors on the charge carrier transport in ternary active layers. The active layers of single charge carrier devices are the same as those of solar cells. The *J*-*V* curves of single charge carrier devices with different PBDT-TS1 doping ratios in donors were measured in dark and are showed in **Fig. 5a** and **5b**.



Fig. 5. (a) $J^{1/2}$ -V curves of hole-only devices; (b) $J^{1/2}$ -V curves of electron-only devices.

Table 2. Hole or electron mobility based on the hole-only or electron-only devices.

PBDT-TS1 (wt%)	μ_h (cm ² /V·s)	μ_e (cm ² /V·s)	μ_{h}/μ_{e}
0	1.53×10 ⁻⁴	7.64×10 ⁻⁵	2.00
20	1.11×10 ⁻⁴	6.25×10 ⁻⁵	1.78
40	8.18×10 ⁻⁵	5.31×10 ⁻⁵	1.54
60	4.84×10 ⁻⁵	4.76×10 ⁻⁵	1.02
80	4.00×10 ⁻⁵	4.40×10 ⁻⁵	0.91
100	2.92×10 ⁻⁵	4.20×10 ⁻⁵	0.70

The charge carrier mobility was calculated according to the space charge limited current (SCLC) method based on the J-V curves of hole-only or electron-only devices. The SCLC is described by the Mott–Gurney equation:

$$J = \frac{9}{8} \varepsilon_r \varepsilon_0 \mu \frac{V^2}{L^3},$$

where ε_0 is the vacuum permittivity, ε_r is the dielectric constant of 3 for common organic materials, μ is the charge carrier mobility, V is the applied voltage, and L is thickness of the active layer.^{7, 42} The calculated hole and electron mobility of all devices are listed in **Table 2**. It is apparent that hole and electron mobility of ternary PSCs are slightly decreased along with the increase of PBDT-TS1 doping ratios in donors. It should be highlighted that hole and

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electron mobility becomes to more balance with $\mu_h/\mu_e \approx 1$ when the PBDT-TS1 doping ratios are about from 60 wt% to 80 wt% in donors. The more balanced hole and electron mobility is beneficial to obtain the relatively high FF and J_{SC} . The high FF can be further illustrated by the shunt resistance (R_{sh}) and series resistance (R_s) of PSCs, as shown in **Table 1**. The R_{sh} is equal to the reciprocal of *J-V* curve slope at J_{SC} point, the reciprocal of J-V curve slope at V_{OC} point represents the R_s of cells. It is apparent that the values of R_{sh} are increased with the increase of PBDT-TS1 doping ratios in donors, the values of Rs are simultaneously decreased. The maximum R_{sh} of 300 Ω cm² and the minimum R_s of 4.9 Ω cm² are obtained for the ternary PSCs with 80 wt% PBDT-TS1 doping ratio in donors, which is beneficial to charge carrier transport and collection for the ternary PSCs. The champion PCE of ternary PSCs with 80 wt% PBDT-TS1 doping ratio in donors can be well explained from the optimized photon harvesting, exciton dissociation, charge carrier transport and collection in the ternary solar cells.

Conclusions

In summary, we have successfully fabricated high efficient parallellinkage ternary PSCs with PTB7:PBDT-TS1 as donors and $PC_{71}BM$ as electron acceptor. The champion PCE achieves 7.91% for ternary PSCs with 80 wt% PBDT-TS1 doping ratio in donors, which corresponds to 12.8% or 28.2% PCE improvement compared with the optimized binary PSCs with PBDT-TS1 or PTB7 as donor. The enhanced PCE should be attributed to synergistic improvement of photon harvesting, exciton dissociation, charge carries transport and collection in ternary blend films. Parallel-linkage structure may be a promising strategy to improve the performance of ternary PSCs, which not only enhances the photon harvesting of the active layers, but also may maintain the efficient bi-continuous interpenetrating network in the ternary active layers.

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Notes and references

- 1. L. Yang, L. Yan and W You, J. Phys. Chem. Lett., 2013, 4, 1802-1810.
- Q. S. An, F. J. Zhang, L. L. Li, J. Wang and Q. Q. Sun, ACS Appl. Mater. Interfaces, 2015, 7, 3691-3698.
- Q. S. An, F. J. Zhang, Q. Q. Sun, J. Wang, L. L. Li, J. Zhang, W. H. Tang and Z. B. Deng, J. Mater. Chem. A, 2015, 3, 16653-16662.
- Y. Z. Lin, Z. G. Zhang, H. T. Bai, J. Y. Wang, Y. H. Yao, Y. F. Li, D. B. Zhu and X. W. Zhan, *Energy Environ. Sci.*, 2015, 8, 610-616.

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- Y. Lin, J. Y. Wang, Z. G. Zhang, H. T. Bai, Y. F. Li, D. B. Zhu and X. W. Zhan, *Adv. Mater.*, 2015, 27, 1170-1174.
- X. W. Zhan, Z. A. Tan, B. Domercq, Z. S. An, X. Zhang, S. Barlow, Y. F. Li, D. B. Zhu, B. Kippelen and S. Marder, *J. Am. Chem. Soc.*, 2007, **129**, 7246-7247.
- S. Foster, F. Deledalle, A. Mitani, T. Kimura, K. B. Kim, T.; Kirchartz, T. Okachi, J. Oguma, K. Miyake and J. R. Durrant, et al. *Adv. Energy Mater.*, 2014, 4, 1400311.
- B. Y. Qi and J. Z. Wang, Phys. Chem. Chem. Phys., 2013, 15, 8972-8982.
- Z. C. He, C. M. Zhong, X. Huang, W. Y. Wong, H. B. Wu, L. W. Chen, S. J. Su and Y. Cao, *Adv. Mater.*, 2011, 23, 4636–4643.
- Y. Liu, F. J. Zhang, H. Dai, W. H. Tang, Z. Wang, J. Wang, A. Tang, H. Peng, Z. Xu and Y. Wang, *Energy Mater. Sol. Cells*, 2013, **118**, 135-140.
- J. B. You, C. C. Chen, Z. R. Hong, K. Yoshimura, K. Ohya, R. Xu, S. L. Ye, J. Gao, G. Li and Y. Yang, *Adv. Mater.*, 2013, 25, 3973-3978.
- F. J. Zhang, X. R. Xu, W. Tang, J. Zhang, Z. Zhuo, J. Wang, Z. Xu and Y. Wang, Sol. Energy Mater. Sol. Cells, 2011, 95, 1785-1799.
- J. D. Chen, C. H. Cui, Y. Q. Li, L. Zhou, Q. D. Ou, C. Li, Y. F. Li and J. X. Tang, *Adv. Mater.*, 2015, 27, 1035-1041.
- C. C. Chen, W. H. Chang, K. Yoshimura, K. Ohya, J. B. You, J. Gao, Z. R. Hong and Y. Yang, *Adv. Mater.*, 2014, 26, 5670–5677.
- M. Zhang, F. J. Zhang, Q. Q. An, Q. Q. Sun, J. Wang, L. L. Li, W. Wang and J. Zhang, *Solar Energy Mater. Sol. Cells*, 2015, 141, 154-161.
- J. B. You, L. T. Dou, K. Yoshimura, T. Kato, K. Ohya, T. Moriarty, K. Emery, C. C. Chen, J. Gao and G. Li, *Nat. Commun.*, 2013, 4, 1446.
- 17. T. Ameri, P. Khoram, J. Min and C. J. Brabec, *Adv. Mater.*, 2013, **25**, 4245-4266.
- S. H. Liu, P. You, J. H. Li, J. Li, C. S. Lee, B. S. Ong, C. Surya and F. Yan, *Energy Environ. Sci.*, 2015, 8, 1463-1470.
- P. Chen, Q. Q. Shi and X.W. Zhan, *Acta Chimica Sinica*, 2015, 73, 252-256.
- P. Chen, Y. Z. Lin, N. K. Zawacka, T. R. Andersen, W. Q. Liu, E. Bundgaard, M. Jørgensen, H. Z. Chen, F. C. Krebs and X. W. Zhan, *J. Mater. Chem. A*, 2014, 2, 19542-19549.
- J. Zhang, Y. Zhang, J. Fang, K. Lu, Z. Wang, W. Ma and Z. J. Wei, Am. Chem. Soc., 2015, 137, 8176–8183.
- V. Gupta, V. Bharti, M. Kumar, S. Chand and A. J. Heeger, *Adv. Mater.*, 2015, 27, 4398–4404.
- P. Cheng, C. Yan, Y. Li, W. Ma and X. W. Zhan, *Energy Environ. Sci.*, 2015, 8, 2357-2364.
- Y. Yang, W. Chen, L. T. Dou, W. H. Chang, H. S. Duan, B.; Li, G. Bob and Y. Yang, *Nat. Photonics*, 2015, 9, 190-198.
- H. Li, Z.-G. Zhang, Y. Li and J. Wang, *Appl. Phys. Lett.*, 2012, 101, 163302.
- P. Cheng, L. Ye, X. A. Zhao, J. H. Hou, Y. F. Li and X. W. Zhan, *Energy Environ. Sci.*, 2014, 7, 1351-1356.
- 27. P. Cheng, Y. Li and X. Zhan, *Energy Environ. Sci.*, 2014, 7, 2005-2011.

- 28. Q. S. An, F. J. Zhang, L. L. Li, Z. L. Zhuo, J. Zhang, W. Tang and F. Teng, *Phys. Chem. Chem. Phys.*, 2014, **16**, 16103-16109.
- F. Machui, S. Rathgeber, N. Li, T. Ameri and C. J. Brabec, J. Mater. Chem., 2012, 22, 15570-15577.
- Q. S. An, F. J. Zhang, L. L. Li, J. Wang, J. Zhang, Z. L. Zhou and W. Tang, ACS Appl. Mater. Interfaces, 2014, 6, 6537-6544.
- B. Ananda Rao, M. Sasi Kumar, G. Sivakumar, S. P. Singh, K. Bhanuprakash, V. J. Rao and G. Sharma, *ACS Sustain. Chem. Eng.*, 2014, 2, 1743-1751.
- 32. S. Liu, P. You, J. Li, J. Li, C.-s. Lee, B. S. Ong, C. Surya and Y. Feng, *Energy Environ. Sci.*, 2015, **8**, 1463-1470.
- L. Y. Lu, W. Chen, T. Xu and L. P. Yu, *Nat. Commun.*, 2015, 6, 7327.
- 34. P. Cheng and X. W. Zhan, *Mater. Horiz.*, 2015, **2**, 462-485.
- L. Yang, H. Zhou, S. C. Price and W. You, J. Am. Chem. Soc., 2012, 134, 5432-5435.
- Y.-J. Hwang, B. A. Courtright and S. A. Jenekhe, Mrs.Commun., 2015, 5, 229-234.
- 37. Y. Y. Liang and L. P. Yu, Acc. Chem. Res., 2010, 43, 1227-1236.
- L. Ye, S. Q. Zhang, W. C. Zhao, H. F. Yao and J. H. Hou, *Chem. Mater.*, 2014, 26, 3603-3605.
- 39. Q. Q. Sun, F. J. Zhang, J. Wang, Q. S. An, C. Zhao, L. L. Li, F. Teng and B. Hu, *J. Mater. Chem. A*, 2015, **3**, 18432-18441
- Q. Q. Sun, F. J. Zhang, Q. S. An, L. L. Li, J. Wang, M. Zhang, W. Wang, F. Teng and J. Zhang, *Org. Electron.*, 2015, 24, 30-36.
- 41. L. Y. Lu, T. Xu, W. Chen, E. S. Landry and L. P. Yu, *Nat. Photonics*, 2014, **8**, 716-722.
- H. Y. Li, L. Duan, D. Q. Zhang and Y. Qiu, J. Phys. Chem. C, 2014, 118, 9990-9995.





we have successfully fabricated high efficient parallel-linkage ternary PSCs with PTB7:PBDT-TS1 as donors and $PC_{71}BM$ as electron acceptor. The champion PCE arrives to 7.91% for ternary PSCs with 80 wt% PBDT-TS1 doping ratio in donors.