



Short Communication

Solvent additive-free ternary polymer solar cells with 16.27% efficiency

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Ternary strategy has been commonly demonstrated as an efficient method to improve the performance of polymer solar cells (PSCs), which has great potential in application of PSCs due to the simple device fabrication. Most of ternary PSCs were designed with complementary absorption spectra of used materials to cover the solar spectrum as wide as possible in order to achieve large short circuit current density (J_{SC}). Recently, over 14% PCE of ternary PSCs have been achieved with narrow bandgap materials as active layers, resulting from the well balanced three photovoltaic parameters [1]. The compatibility of used materials plays a vital role in optimizing phase separation degree of ternary active layers as morphology regulator [2,3]. An up-side-down annealing treatment has been proposed in Ref. [3]. The well optimized phase separation degree can recombine the advantages of used materials into one cell through energy transfer, charge transfer, cascade energy levels or alloyed states. Some new experimental methods have been developed to further investigate the dynamic process between two donors or two acceptors. The current density versus voltage (J - V) curves of PSCs without donor or acceptor were used to investigate exciton dynamic process [4]. The charge transport process in ternary active layers can be investigated according to the J - V curves of ternary PSCs covered with a specific optical filter [3]. The photogenerated exciton distribution in active layers can be optimized by altering the content of third component, which is beneficial to improve the balance of charge transport and collection in ternary PSCs [5]. Meanwhile, the stability of PSCs can also be improved by employing ternary strategy due to the well optimized phase separation of ternary active layers [4,6].

Recently, Yuan et al. [7] reported a 15.7% PCE of binary PSCs with PM6 as donor and new non-fullerene Y6 as acceptor, and the PM6:Y6 based active layers were well optimized with solvent additive and post annealing treatment. Fan et al. [8] reported a 16.02% PCE of binary PSCs with P2F-Ehp:Y6 as active layers with

solvent additive and post annealing treatment. In this work, a record PCE of 16.27% is achieved in solvent additive-free ternary PSCs, the corresponding PM6:Y6 and PM6:IT-4F binary PSCs exhibit PCEs of 15.35% and 12.76%, respectively. The fill factor (FF) and open circuit voltage (V_{OC}) of PM6:IT-4F based binary PSCs are 75.1% and 0.860 V, which are slightly larger than 73.2% and 0.836 V of PM6:Y6 based binary PSCs. Over 73% FFs of two binary PSCs indicate the good compatibility of used materials, which may provide more potential to prepare efficient ternary PSCs by recombining the advantages of two binary PSCs [9]. The optimized ternary PSCs with 20 wt% IT-4F in acceptors exhibit a 16.27% PCE, resulting from the simultaneously enhanced J_{SC} of 25.40 mA cm⁻², V_{OC} of 0.844 V and FF of 75.9%. It should be highlighted that all active layers were treated with carbon disulfide (CS₂) vapor about 40 s. The experimental details are described in the [Supplementary data](#). To the best of our knowledge, the 16.27% PCE of ternary PSCs should be the largest values, especially for PSCs without solvent additives. The schematic diagram of PSCs and chemical structures of used materials are exhibited in [Fig. S1 \(online\)](#).

The apparent complementary absorption spectra of neat PM6, Y6 and IT-4F films can be observed in [Fig. 1a](#). The photon harvesting of blend films should be enhanced by incorporating appropriate IT-4F, especially in the spectral range from 650 to 750 nm. The current density versus voltage (J - V) curves of PSCs were measured under AM 1.5 G illumination at intensity of 100 mW cm⁻², as exhibited in [Fig. 1b](#). Apparently, J_{SC} s of ternary PSCs can be increased for IT-4F content up to 20 wt% in acceptors, which should result from the enhanced photon harvesting by IT-4F in the ternary active layers. The external quantum efficiency (EQE) spectra of PSCs are shown in [Fig. 1c](#). There is an apparent dip of EQE spectra of PM6:Y6 based binary PSCs, which can be well compensated by incorporating IT-4F in acceptors. The optimized ternary PSCs exhibit more flat EQE spectra in the whole spectral range. The integrated J_{SC} based on the EQE spectrum is 24.57 mA cm⁻² for the optimized ternary PSCs, which matches well with the measured J_{SC} value. The slightly blue-shifted EQE spectral edge of tern-

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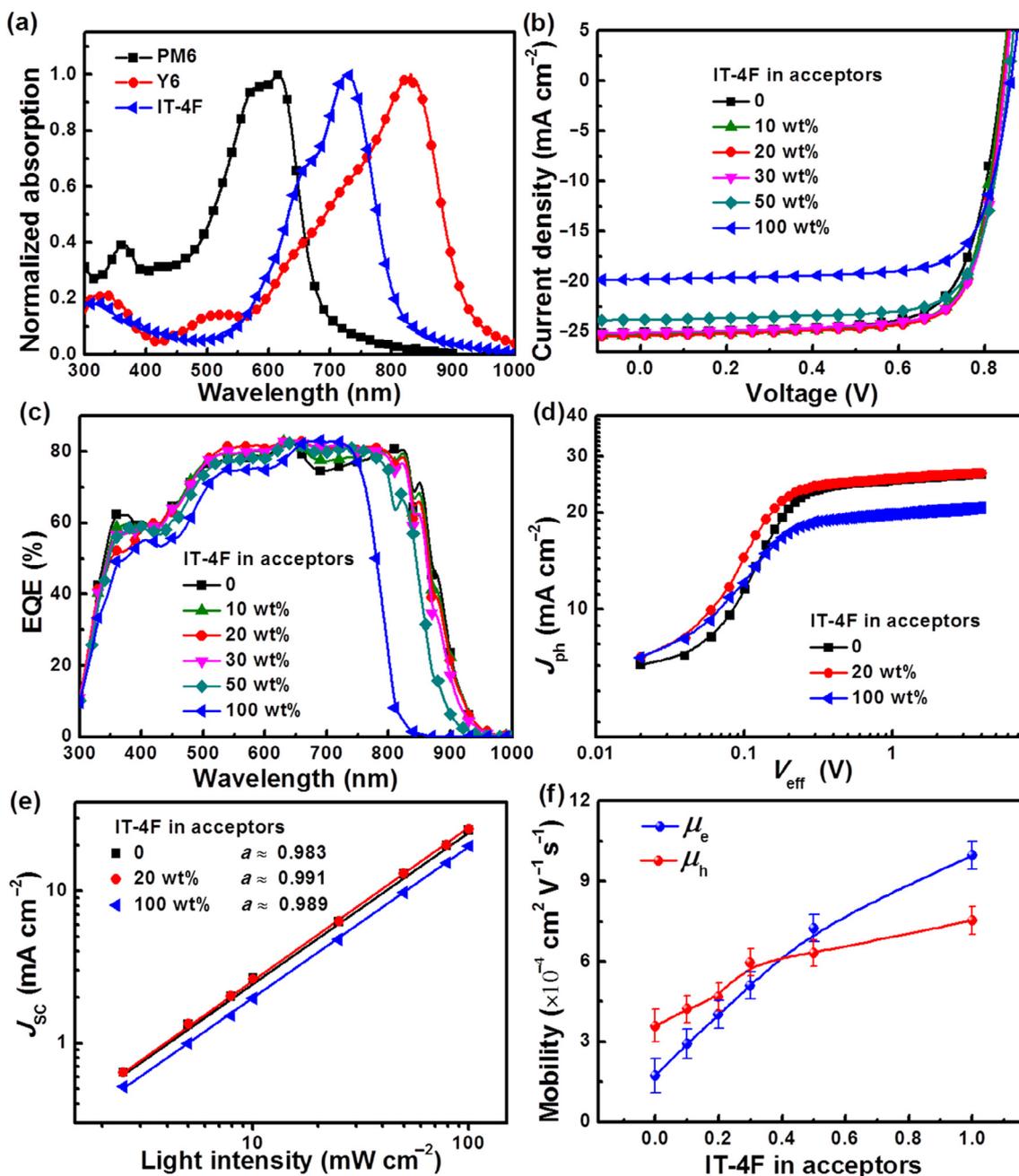


Fig. 1. (Color online) Ternary polymer solar cells with 16.27% PCE. (a) Absorption spectra of neat films. (b) J - V curves and (c) EQE spectra of PSCs. (d) J_{ph} - V_{eff} curves of the typical PSCs. (e) J_{sc} dependence on light intensity of the typical PSCs. (f) Charge mobility in PSCs with different IT-4F content in acceptors.

Table 1
Photovoltaic parameters of PSCs with different IT-4F content in acceptors.

IT-4F (wt%)	J_{sc} (mA cm^{-2})	FF (%)	V_{oc} (V)	PCE (%)	
				Max	Avg ^a
0	25.08	73.2	0.836	15.35	15.21 ± 0.11
10	25.26	75.3	0.840	15.99	15.86 ± 0.08
20	25.40	75.9	0.844	16.27	16.14 ± 0.09
30	25.07	75.8	0.848	16.11	15.93 ± 0.12
50	23.80	75.4	0.855	15.34	15.19 ± 0.12
100	19.75	75.1	0.860	12.76	12.62 ± 0.07

^a Average PCEs and the deviations based on 20 cells prepared from different batches.

ary PSCs is observed along with IT-4F content increasing. The optimized photon harvesting should be achieved in the ternary active layers with 20 wt% IT-4F in acceptors, which can well explain the

maximum J_{sc} of the optimized ternary PSCs. The detailed photovoltaic parameters of PSCs are summarized in Table 1. In addition to absorption spectral complementation of used materials, two

binary PSCs also exhibit the complementary photovoltaic parameters. The V_{OC} s of ternary PSCs are monotonously increased along with IT-4F content increasing, indicating that working mechanism of ternary PSCs should be alloyed model due to the good compatibility of used materials [10].

The photogenerated current density (J_{ph}) dependence on the effective bias (V_{eff}) of the typical PSCs is shown in Fig. 1d and the corresponding parameters are listed in Table S1 (online). The J_{ph} of the optimized ternary PSCs rapidly gets into the saturated state under low V_{eff} , indicating the more efficient charge transport and collection in the ternary active layers. The more efficient charge transport in the ternary active layers can be further confirmed from relatively large FF of the optimized ternary PSCs. Meanwhile, saturated J_{ph} of the optimized ternary PSCs is slightly larger than that of two binary PSCs, which well accords with the J_{SC} s of the typical PSCs. Fig. S2 (online) shows the J - V curves of typical PSCs under different light intensity. The dependence of the J_{SC} on light intensity is exhibited in Fig. 1e. The correlation between J_{SC} and light intensity (P_{in}) can be expressed as $J_{SC} \propto P_{in}^\alpha$, where α is close to 1 when the bimolecular recombination could be negligible. The α values are 0.983, 0.991 and 0.989 for PM6:Y6 based, the optimized ternary and PM6:IT-4F PSCs, respectively. The relatively large α approaching to unit suggests the suppressed bimolecular recombination in optimized ternary active layers, which also well accords with the relatively high FF of the optimized ternary PSCs. The space charge limited current (SCLC) model was employed to estimate charge mobility in different blend films (Fig. S3 and Table S2 online). The electron mobility (μ_e) and hole mobility (μ_h) values dependence on IT-4F content are described in Fig. 1f. The ternary PSCs with 20 wt% IT-4F in acceptors exhibit relatively balanced charge mobility, resulting in enhanced FFs of ternary PSCs in comparison with the two binary PSCs.

In summary, 16.27% PCE is achieved from solvent additive-free ternary PSCs with PM6:Y6:IT-4F as the active layers contenting 20 wt% IT-4F in acceptors, resulting from the simultaneously enhanced J_{SC} of 25.40 mA cm⁻², V_{OC} of 0.844 V and FF of 75.9%. Approximate 5.9% PCE improvement can be obtained in comparison with PM6:Y6 based binary OSCs by employing ternary strategy, especially for the active layers without solvent additive. This work further demonstrates that ternary PSCs should be among the best candidates for organic photovoltaic industrialization with very simple fabrication process.

Conflict of interest

The authors declare that they have no conflict of interest.

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Author contributions

Fujun Zhang proposed the research and directed the study. Qiaoshi An carried out the materials selection, cells fabrication

and characterizations. Fujun Zhang, Qiaoshi An, Xiaoling Ma and Jinhua Gao analyzed the data and prepared the manuscript.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scib.2019.03.024>.

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