

Dual Sensitizer and Processing-aid Behavior of Donor Enables Efficient Ternary Organic Solar Cells

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Summary

Herein, we report ternary organic solar cells with a power conversion efficiency (PCE) of 14.0%. By incorporating 10 wt% of BIT-4F-T in the PTB7-Th:IEICO-4F blend, we obtain an enhancement of all photovoltaic parameters compared to the binary devices leading to a 15% performance improvement in ternary blend. The high photocurrent in 10% BIT-4F-T blend, results from a complementary absorption profile of donor components and a hole transfer from BIT-4F-T to PTB7-Th. Morphological and device characterizations reveal that the addition of 10% BIT-4F-T acts not only as a sensitizer but also as a solid processing-aid, which is beneficial for charge generation and transport. The effect of the third component is observed in different non-fullerene and fullerene OSCs. Our study demonstrates that careful selection of a third component, where dual sensitizing and processing-aid effects are observed, can be a design strategy to achieve a concomitant improvement in all photovoltaic parameters.

Introduction

The development of bulk-heterojunction (BHJ) organic solar cells (OSCs) has set a new horizon with newly emerged small molecule acceptors (SMAs) that are not fullerene derivatives. SMAs based solar cells have been proven to outperform devices based on fullerene derivatives (such as PC₆₁BM, PC₇₁BM or ICBA),¹⁻⁴ owing to the tunable absorption range of SMAs with band gap engineering and low non-radiative recombination.⁵⁻⁸ Along with interface engineering where fill factor (FF) values reached up to 80%, record power conversion efficiencies (PCEs) exceeding 14% have been achieved in single junction binary BHJ devices.⁹⁻¹¹ Recently, a low band gap small molecule acceptor consisting of indacenodithiophene (IDT) core flanked with fluorinated 2-(3-oxo-2,3-dihydroinden-1-ylidene)malononitrile, IEICO-4F (1.25 eV), has shown a short-circuit current (J_{sc}) of up to 27 mA cm⁻² in OSCs with commonly known donor PTB7-Th. This shows the potential of SMAs to achieve an ultra-high photocurrent and thus, it motivates the OPV field to improve the remaining photovoltaic parameters to further boost their performance.¹²⁻¹⁴

Between the strategies to further improve the PCE of BHJ-OSCs, e. g. tandem architectures,¹⁵ the addition of a third component is proven to be a promising method because of the easy fabrication in a single junction architecture.¹⁶⁻¹⁹ The third component (i.e. either a second donor D₂, or a second acceptor A₂) is used in minority amounts compared to the existing binary donor:acceptor (D₁:A₁) materials to form a ternary mixture. Depending on the photon harvesting capabilities, this third component (can be a small molecule or polymer) can sensitize a different part of the solar spectrum compared to the binary D₁:A₁, which then contributes to the photocurrent, or can be energetically aligned to improve the open-circuit voltage (V_{oc}) in the ternary devices.²⁰ Carefully selecting and incorporating a third component can also improve the solid-state morphology of the binary components, and thus, act as a processing-aid; this strategy has been shown in previous reports to benefit FF.^{21,22} Although it

is relatively easy to select a third component which satisfies one of these two criteria; the formation of optimal nano-morphology and subsequent improvement of all photovoltaic parameters is non-trivial.

In this work, we report a general design strategy for ternary solar cells where the third component simultaneously improves all the photovoltaic parameters as compared to their binary counterparts. A small molecule donor consisting of IDT core coupled with thiophene and difluorobenzothiadiazole, BIT-4F-T, has been carefully chosen as a third component into PTB7-Th binary blends with numerous acceptors with a number of reasons²³: 1) BIT-4F-T has a deeper ionization potential (IP) level than that of PTB7-Th (used as donor in this study for binary devices), allowing V_{oc} modulation;²⁴ 2) in fullerene binary solar cells, using BIT-4F-T has shown to suppress geminate recombination; and 3) it possesses a semi-crystalline nature compared to PTB7-Th, which is proven to be useful in improving the molecular packing of the donor PTB7-Th in the ternary system and thus, BIT-4F-T aids the processing for an optimal nanomorphology.²⁵ Indeed, grazing incidence wide-angle x-ray scattering (GIWAXS) patterns show that the optimal content of BIT-4F-T (10 wt%) in PTB7-Th:IEICO-4F binary blend acts as a solid processing-aid that not only decreases the π - π stacking distance of PTB7-Th, but also increases the alkyl stacking coherence length of PTB7-Th when compared to its binary counterpart and thus, improves the overall nanoscale morphology.²⁶ Furthermore, adding 10 wt% BIT-4F-T sensitizes photons in the range of 400 nm to 600 nm, facilitates more efficient charge generation and extraction, and reduces both the geminate and non-geminate recombination. Finally, V_{oc} of the ternary devices improved gradually upon addition of BIT-4F-T due to an IP shift in the blend films. All these improvements yield a J_{sc} of 27.3 mA cm⁻², FF of 70.9 % and a V_{oc} of 723 mV in the best devices with a power conversion efficiency (PCE) of 14.0 %, where concomitant improvement in photovoltaic parameters is observed compared to its binary counterparts. A series of ternary devices with BIT-4F-T were also fabricated with different SMAs including IEICO-4Cl, IEICO and

fullerene derivative PC₇₁BM showed a similar trend, suggesting a good generality with this third component for efficient ternary devices.

Results and Discussion

To investigate the photovoltaic performance of the ternary blends, the OSC devices are constructed in inverted architecture with ITO/ZnO(~35 nm)/Active Layer (~150 nm)/MoO_x(~7nm)/Ag(~100 nm) (**Figure 1a**). **Figure 1b** and **c** show the chemical structures of the materials and their respective normalized absorbance profiles. As depicted from **Figure 1c**, BIT-4F-T, PTB7-Th and IEICO-4F has an absorption range from 350 nm to 1000 nm, demonstrating the potential for harvesting more photons compared with PTB7-Th:IEICO-4F binary films.²⁷ Moreover, the optimized ternary blend films exhibit a higher absorption strength than that of the binary system, suggesting improved nanoscale morphology which can be translated as photocurrent (**Figure 2a**).^{28,29}

Table 1. Key photovoltaic parameters of binary PTB7-Th:IEICO-4F (0% BIT-4F-T) and ternary PTB7-Th:BIT-4F-T:IEICO-4F (0.9:0.1:1, 10% BIT-4F-T) and PTB7-Th:BIT-4F-T:IEICO-4F (20% BIT-4F-T), extracted from the *J-V* curves at 100 mW cm⁻² illumination.

Blend Film	J_{sc} (mA cm ⁻²)	V_{oc} (mV)	FF (%)	PCE (%)	Ave PCE (%) ^a
0% BIT-4F-T	26.7	713	65.1	12.4	11.8
10% BIT-4F-T	27.4	720	69.2	13.7	13.2
10% BIT-4F-T ^b	27.3	723	70.9	14.0	13.6
20% BIT-4F-T	24.1	728	64.7	11.4	10.7

a: Average values obtained from 30 devices. b: using conventional architecture with the layer stack of ITO/PEDOT:PSS:WO_x/Active layer/DPO/Ag.

Figure 2b depicts the current density-voltage (J - V) characteristics of PTB7-Th:IEICO-4F and PTB7-Th:BIT-4F-T:IEICO-4F devices under simulated AM 1.5G solar irradiance (100 mW cm^{-2}) and **Table 1** summarizes the key photovoltaic parameters of the corresponding photovoltaic devices. Binary PTB7-Th:IEICO-4F (called 0% BIT-4F-T in this work) devices yield a PCE of 12.4% with the J_{sc} of 26.7 mA cm^{-2} , V_{oc} of 713 mV and FF of 65.1% , similar to the previously reported performance.¹³ Interestingly, the PTB7-Th:BIT-4F-T: IEICO-4F (0.9:0.1:1, called 10% BIT-4F-T in this work) ternary device exhibits the champion performance with concomitant increase in all the PV parameters up to 27.4 mA cm^{-2} J_{sc} , 720 mV V_{oc} and a FF of 69.2 % with efficiency of 13.7%. However, further increasing the amount of the third component (0.8:0.2:1, called 20% BIT-4F-T in this work, more details of the different ratios are depicted in **Figure S1a** and **Table S1**), in fact, results in a decrease of J_{sc} and FF, while V_{oc} is slightly increased. In order to explain the increase in V_{oc} as a function of BIT-4F-T addition, we carried out photoelectron spectroscopy in air (PESA) measurements, where the IP of the two donor mixtures were tracked (**Figure S2**).³⁰ We observed that the IP of the donor blend is shifted to a higher energy values (shifted down), which is in line with the increasing V_{oc} in ternary devices upon BIT-4F-T addition.^{30,31}

Recently, Zhou and co-workers reported that mixing tungsten oxide (WO_x) nanoparticles with PEDOT:PSS emulsion as a hybrid hole-transporting layer (HTL) is an efficient strategy to significantly improve the FF in organic solar cells.¹¹ To further enhance our ternary device performance, we utilized this hybrid HTL composites (PEDOT:PSS: WO_x , 1:1 volume ratio) to construct the normal device configuration of ITO/HTL (~40 nm)/Active layer(~150 nm)/ phenyl(2- naphthyl)diphenylphosphine oxide (DPO) (~5 nm)/Ag(~100 nm), where DPO is the cathode modification layer.³² As shown in **Figure S3**, **Table 1** and **Table S2**, benefiting from the advantages of PEDOT:PSS: WO_x HTL, the best PCE of 10% BIT-4F-T ternary blend devices is up to 14.0% with the modified HTL, along with a 27.3 mA cm^{-2} J_{sc} , 723 mV V_{oc} and 70.9% FF, an enhancement of 15% in comparison with the binary blend

counterpart (12.1%). The PCE distribution from 30 devices (from different fabrication batches) for binary and ternary devices is represented in **Figure S4**, represents a good reproducibility of this ternary system.

The external quantum efficiency (EQE) measurements are performed to study the light-to-current conversion of binary and ternary devices. The integrated J_{sc} values from the EQE traces matches the current densities extracted from the J - V curves with a margin of less than 10%. As shown in **Figure 2c**, 10% BIT-4F-T ternary devices depict slightly higher EQE compared to the binary devices, whereas higher loading of BIT-4F-T decreases the photocurrent (**Figure S1b**). To verify our high photocurrent, we calculated the internal quantum efficiency (IQE) for binary and ternary blends. A maximum IQE value of over 90% was observed between 600–620 nm in both the binary and ternary systems. (**Figure S5b**). We clearly observe that IQE is higher in the ternary system, especially in the spectral region where IEICO-4F absorbs, demonstrating that the orientation/nanostructure of IEICO-4F is also improved upon addition of BIT-4F-T. These findings are consistent with the results from the GIWAXS characterization (discussed below), suggesting more efficient photon-to-charge carrier conversion and carrier collection at the electrodes for the ternary devices.

The different light-to-photon conversion capabilities of ternary devices are displayed in **Figure 2d**, by taking the ΔEQE (defined as $EQE_{ternary} - EQE_{binary}$),^{33–35} into account. In this representation, we can clearly see the contribution of 10% BIT-4F-T to current generation at ~ 400 nm and between 500-600 nm, which is due to the charge transfer from BIT-4F-T to PTB7-Th. To verify this hole transfer, we fabricated hole-only bilayer devices with a configuration of ITO/PEDOT/BIT-4F-T/PTB7-Th/MoO_x/Ag (**Figure 3a**). This method has proven particularly useful for revealing the electronic processes in ternary blends, without the need of ultra-fast techniques, such as transient absorption spectroscopy.^{15,21} The asymmetric behaviour of the corresponding J - V curve demonstrates a hole transfer occurs from BIT-4F-T to PTB7-Th, which is in line with the energetic levels where the IP of BIT-4F-T lies lower

than that of PTB7-Th (**Figure S6**), with the enhanced light to current conversion in the 500-600 nm range. However, this process would not be the sole reason for the increase in EQE over the whole region as shown in **Figure 2d**. BIT-4F-T also facilitates an optimal nanoscale morphology, which is in agreement with the absorbance profiles and the enhanced EQE in the 650-1000 nm (discussed in the following section).³⁶

To get a deeper insight into the recombination and transport processes in binary and ternary devices, we investigate the J - V curves as a function of light intensity to obtain initial information on the non-geminate recombination (bimolecular and trap-assisted recombination). In general, a slope of kT/q is expected for bimolecular recombination (where k is Boltzmann constant, q is elementary charge and T is temperature) in the plot of V_{oc} versus the natural logarithm of the light intensity.^{13,37} Differently, a signature of trap assisted recombination is pronounced by an enhanced dependence of V_{oc} with light intensity ($2 kT/q$). As shown in **Figure 3b**, PTB7-Th:IEICO-4F binary device (0% of BIT-4F-T) delivers a slope of $1.26 kT/q$, suggesting a deviation from the linearity originated from traps.¹³ The trap assisted recombination is drastically reduced upon addition of 10% of BIT-4F-T (slope $1.09 kT/q$), in agreement with the higher FF and better performance obtained in the ternary device. On the other hand, higher loading of BIT-4F-T (more than 10%) have a detrimental effect on charge recombination, depicted by a higher deviation from the linearity (slope $1.30 kT/q$).¹² Reduced trap-assisted recombination in 10% BIT-4F-T devices should facilitate the charge dynamics of the binary system. To demonstrate that, the photocurrent density (J_{ph}) as a function of the effective voltage (V_{eff}) are plotted in **Figure 3c**.³⁸ In this figure, J_{ph} is defined as $J_{ph} = J_L - J_D$, where J_L and J_D are the current density measured in the light and in the dark, respectively, whereas V_{eff} is given by $V_{eff} = V_0 - V$, where V_0 and V are the displacement and applied voltage, respectively. In 10% ternary device, J_{ph} quickly saturates around $V_{eff} \sim 0.3V$, whereas both binary and 20% ternary devices depict a stronger field-dependent extraction. It

is worth to mention that in the extraction condition, in which we assume that all the photo-generated hole-electron pairs are dissociated into free charges and collected in their respective electrodes, the saturation current density (J_{sat}) is only limited by the absorbed photons. Therefore, calculating J_{sat} allows the estimation of the maximum rate of free charge carrier generation (G_{max}) according to the equation: $J_{sat} = G_{max}qL$, where q and L are the elementary charge and active layer thickness, respectively. We find G_{max} values of $1.58 \times 10^{22} \text{ cm}^{-3} \text{ s}^{-1}$, $1.83 \times 10^{22} \text{ cm}^{-3} \text{ s}^{-1}$ and $1.29 \times 10^{22} \text{ cm}^{-3} \text{ s}^{-1}$ for 0% (binary), 10% and 20% ternary devices, respectively; in line with the trend of J_{sc} values calculated.^{39,40} A similar trend is also observed when considering charge generation at maximum power point of the $J-V$ curves (G_{mpp}) and in short-circuit condition (G_{sc}). The 10% BIT-4F-T ternary device enhances both G_{mpp} (72%) and G_{sc} (91%) compared to that of binary ($G_{mpp} = 62\%$ and $G_{sc} = 89\%$) and 20% ternary devices ($G_{mpp} = 60\%$ and $G_{sc} = 85\%$). These results further confirm that addition of 10% of the third component facilitates charge dissociation and extraction, leading to enhanced FF and J_{sc} for ternary solar cells.⁴¹

In parallel, we perform charge extraction (CE) measurements to understand the recombination mechanisms.⁴² This technique allows the calculation of the charge carrier density (n) by monitoring the evolution of charges from V_{oc} to J_{sc} conditions. As presented in **Figure 3d**, 10% ternary device exhibits the highest charge density ($n = 2.09 \times 10^{16} \text{ cm}^{-3}$) compared to binary ($n = 1.69 \times 10^{16} \text{ cm}^{-3}$) and 20% ternary ($n = 1.22 \times 10^{16} \text{ cm}^{-3}$) devices. The improved n in 10% ternary based devices well corroborates with the increased light to current conversion of the ternary devices, whereas trap assisted recombination observed for 0% BIT-4F-T and 20% BIT-4F-T blends results in a reduced charge extraction. In order to quantify the transport behaviours of the binary and ternary devices, we investigate the charge carrier mobility by photo-induced charge carrier extraction by linearly increasing voltage (photo-CELIV).⁴³ Photo-CELIV traces of binary and ternary solar cells (**Figure S7**) shows similar charge carrier mobilities in the range of $4\text{-}5 \times 10^{-4} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, however, PTB7-Th:IEICO-4F

displays a broader extraction peak compared to 10% ternary, suggesting a more dispersive transport behaviour.

So far, we provide evidence of different non-geminate recombination in binary and ternary devices, we now focus on geminate recombination to understand how charge photogeneration is influenced in the ternary devices resulting in high J_{sc} values. To understand this, we employ time delayed collection field (TDCF) technique to calculate the total extracted charge (Q_{tot}) at different pre-biased voltages.^{44,45} TDCF measurements reveal that the total extracted charges for 10% BIT-4F-T ternary device are field-independent whereas in binary blends Q_{tot} depicts a field-dependent behaviour (**Figure S8**). These results suggest that introducing only a low amount of BIT-4F-T not only improves the charge transport, but also reduces the geminate recombination of PTB7-Th:IEICO-4F system, yielding a J_{sc} of 27.3 mA cm⁻² and a FF of 70% in the best devices.

To fully understand the role of this third component (BIT-4F-T) on the performance improvement, we studied the active layer microstructure by probing the crystallinity and molecular packing using grazing-incident wide-angle X-ray scattering (GIWAXS) measurements.^{46,47} Firstly, as shown in **Figure 4a-c**, with the binary and both the ternary samples exhibiting π - π stacking peaks in the out of plane (OOP) direction, the molecular packing of both the donor moieties remain predominantly face-on oriented with respect to the substrate surface (similar to the neat films shown in supporting **Figure S9**).^{29,48} Next, in order to understand the BIT-4F-T as a processing aid in details, we thoroughly analysed the GIWAXS data, and discerned the impact of individual component on the overall morphology. This was done by taking line-cuts from the GIWAXS patterns in the OOP direction (**Figure 4d**) and by assigning OOP peaks to individual components, see the supporting information for the details of the peak fit analysis.^{49,50} This comprehensive analysis enabled us to separate the scattering intensity of the BIT-4F-T peak in the ternary systems, and thus, to measure the impact of BIT-4F-T on the packing motif of the donor PTB7-Th. Remarkably, we found that

not only the d-spacing of PTB7-Th (π - π stacking) decreases (**Figure 4e**) but also its coherence length increases (**Figure 4f**) when 10% BIT-4F-T was loaded to the binary system.^{51,52} However, in the 20% BIT-4F-T sample, the d-spacing increases slightly with a slight decrease in the coherence length, showing that the addition of BIT-4F-T is optimal in the 10%-BIT-4F-T sample. Furthermore, in order to establish a correlation between this change in the PTB7-Th π - π stacking d-spacing (and coherence length), the respective device PCEs of the binary and ternary samples are also plotted in **Figure 4e, f**, showing an excellent agreement. We also plotted BIT-4F-T scattering intensity *versus* sample (**Figure S12**), normalised to the binary system where the scattering intensity of the BIT-4F-T was taken to be zero. While in general all the samples exhibit mostly an amorphous nature in solid film morphology,^{53,54} and also comparing scattering from a three-component ternary system to a two-component binary system is not straightforward, this plot nonetheless shows that the 10% BIT-4F-T sample exhibits slightly higher scattering intensity than its 20% counterpart, revealing that 10% sample indeed offers an locally optimized para-crystalline morphology that results in the highest PCE. This is further evaluated with the analysis of the effect of BIT-4F-T loading on the IEICO-4F molecular packing. Similar to the effect of BIT-4F-T on PTB7-Th, addition of 10% BIT-4F-T decreases the π - π stacking of IEICO-4F and increases the coherence length, followed by an increase of the π - π stacking and a small decrease of the coherence length with further loading of BIT-4F-T to 20% (**Figure S13**). Taken together, the GIWAXS data demonstrates that BIT-4F-T acts as a solid processing-aid in the optimal blend, facilitating an increased ordering of the donor polymer and acceptor in the ternary morphology. The morphological features of blend films were also characterized via transmission electron microscopy (TEM) and atomic force microscopy (AFM) (**Figure S14**). The TEM images of the optimal ternary blend is featureless, suggesting a mixed phase in micro-scale and smooth with the root-mean-square (RMS) of 2.12 nm from AFM.

Until now, we have shown the concomitant improvement in ternary devices using a third component, BIT-4F-T, in PTB7-Th:IEICO-4F system. Encouraged by this, we incorporated BIT-4F-T (10 wt%) into various binary blends using different acceptors, namely PTB7-Th:PC₇₁BM, PTB7-Th:IEICO, PTB7-Th:IEICO-4Cl. The molecular structures of the acceptors are depicted in **Figure S15-S17**. As shown in **Figure 5a-5c** and **Table S3-S5**, the PCE of all ternary blends were improved from 9.09% to 10.3%, 5.58% to 6.58% and from 10.2% to 11.7% in PTB7-Th:PC₇₁BM, PTB7-Th:IEICO, PTB7-Th:IEICO-4Cl, respectively.⁵⁵ These improvements are consistent with the ones observed in PTB7-Th:IEICO-4F blend, strongly supporting the general applicability of BIT-4F-T serving as an efficient third component to improve the photovoltaic performance, including fullerene and non-fullerene OSCs.

To move the organic photovoltaics field forward, highly efficient devices should retain their performances when different stress tests are applied. For this reason, we tested the photovoltaic performance of the best ternary blends with respect to their binary counterparts as a function of time under light (1 sun illumination, N₂), thermal stress (80 degrees °C, N₂) and shelf-life in nitrogen conditions (**Figure 6a-c**). More details of all photovoltaic parameters (J_{sc} , V_{oc} and FF) as a function of time for binary and ternary solar cells are plotted in **Figure S18-20**. We exposed the binary and ternary devices at operating condition (AM1.5 radiation to illumination 100 mW cm⁻²) for more than 500 hours (**Figure 6a**). A severe burn-in, referred to large PCE drop in the first 50 hours of light exposure, is observed. After, ternary devices retained over 60% of their initial performance for 500 hours. In contrast, the binary devices performance is reduce to 50% of their initial values. In addition, we also tested the shelf-lifetime (dark, room temperature, nitrogen atmosphere) and thermal-stability (dark, 80 °C, nitrogen atmosphere) for more than 20 days. As presented in **Figure 6b** and **c**, after 480 hours, the ternary devices retain 85% of their initial performance, whereas binary devices

performances retain < 80% of their initial value. These stability measurements suggest that the addition of BIT-4F-T to PTB7-Th:IEICO-4F blend not only improves photovoltaic performance but also has a synergistic benefit on both storage lifetime and photo-stability, which demonstrates a significant advantage for practical applications of our ternary system.

Conclusion

In conclusion, a general design strategy for efficient ternary solar cells is highlighted using a dual acting third component small molecule donor BIT-4F-T. We find that adding 10% BIT-4F-T increases the absorption window of the photoactive layers due to its complementary absorption. Hole only devices exhibit that BIT-4F-T contributes to the photocurrent via hole transfer to PTB7-Th. Moreover, BIT-4F-T also functions as a processing-aid in the ternary systems, increasing the overall volume fraction of the highly ordered region, and thus, improves the charge generation and transport. This dual sensitizer and processing aid character of BIT-4F-T along with interface engineering yields 14% ternary PTB7-Th:BIT-4F-T:IEICO-4F devices with J_{sc} of 27.3 mA cm⁻² and FF of 70.9%. The unique behaviour of BIT-4F-T is also proven with other SMA ternary solar cells as well as fullerene based devices, which demonstrates the novelty of this small molecule donor to realize high efficiency ternary solar cells. Overall, our results reveal a guideline for a D₂ moiety that can be used for improving all the photovoltaic parameters simultaneously in ternary devices. This strategy would pave a way to develop device architectures for commercially viable organic photovoltaics.

Authors Contributions

X. S. and N.G. conceived and developed the ideas. J.-L. W. supplied BIT-4F-T. X. S. designed the experiments and performed device fabrication. N. G. did the electrical characterization and data analyses. M. M. N. and H. A. performed GIWAXS measurements and analyses. S.H.K. Paleti performed ellipsometry measurements. X. S., N. G. and D.B. wrote the manuscript. This project was supervised by D.B.

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Declaration of interests

The authors declare no competing interests.

References

- (1) Baran, D.; Gasparini, N., Wadsworth, A. , Tan, C. H.; Wehbe, N. , Song, X. , Hamid, Z. , Zhang, W. , Neophytou, M. , Kirchartz, T. , et al. , (2018). Robust Nonfullerene Solar Cells Approaching Unity External Quantum Efficiency Enabled by Suppression

- of Geminate Recombination. *Nature Commun.* 9, 2059.
- (2) Günes, S. , Baran, D. , Günbas, G. , Özyurt, F. , Fuchsbauer, A. , Sariciftci, N. S. , and Toppare, L. (2008). Photovoltaic and Photophysical Properties of a Novel Bis-3-Hexylthiophene Substituted Quinoxaline Derivative. *Sol. Energy Mater. Sol. Cells* 92, 1162–1169.
 - (3) Baran, D. , Kirchartz, T. , Wheeler, S. , Dimitrov, S. , Abdelsamie, M. , Gorman, J. , Ashraf, R. S. , Holliday, S. , Wadsworth, A. , Gasparini, N. , et al. , (2016). Reduced Voltage Losses Yield 10% Efficient Fullerene Free Organic Solar Cells with voltage > 1 V Open Circuit Voltages. *Energy Environ. Sci.* 9, 3783–3793.
 - (4) Du, X. , Heumueller, T. , Gruber, W. , Classen, A. , Unruh, T. , Li, N. , and Brabec, C. J. (2018). Efficient Polymer Solar Cells Based on Non-Fullerene Acceptors with Potential Device Lifetime Approaching 10 Years. *Joule* DOI: 10.1016/j.joule.2018.09.001.
 - (5) Tang, A. , Xiao, B. , Wang, Y. , Gao, F. , Tajima, K. , Bin, H. , Zhang, Z.-G. , Li, Y. , Wei, Z. , and Zhou, E. , (2018). Simultaneously Achieved High Open-Circuit Voltage and Efficient Charge Generation by Fine-Tuning Charge-Transfer Driving Force in Nonfullerene Polymer Solar Cells. *Adv. Funct. Mater.* 28, 1704507.
 - (6) Chen, S. , Liu, Y. , Zhang, L. , Chow, P. C. Y. , Wang, Z. , Zhang, G. , Ma, W. , and Yan, H. (2017). A Wide-Bandgap Donor Polymer for Highly Efficient Non-Fullerene Organic Solar Cells with a Small Voltage Loss. *J. Am. Chem. Soc.* 139, 6298–6301.
 - (7) Liu, J. , Chen, S. , Qian, D. , Gautam, B. , Yang, G. , Zhao, J. , Bergqvist, J. , Zhang, F. , Ma, W. , Ade, H. , et al., (2016). Fast Charge Separation in a Non-Fullerene Organic Solar Cell with a Small Driving Force. *Nature Energy.* 1, 16089.
 - (8) Lopez, S. A. , Sanchez-Lengeling, B. , de Goes Soares, J. , and Aspuru-Guzik, A. (2017). Design Principles and Top Non-Fullerene Acceptor Candidates for Organic Photovoltaics. *Joule* 1, 857–870.

- (9) Zhang, S. , Qin, Y. , Zhu, J. , and Hou, J. , (2018). Over 14% Efficiency in Polymer Solar Cells Enabled by a Chlorinated Polymer Donor. *Adv. Mater.* 30, 1800868.
- (10) Li, S. , Ye, L. , Zhao, W. , Yan, H. , Yang, B. , Liu, D. , Li, W. , Ade, H. , and Hou, J. (2018). A Wide Band Gap Polymer with a Deep Highest Occupied Molecular Orbital Level Enables 14.2% Efficiency in Polymer Solar Cells. *J. Am. Chem. Soc.* 140, 7159–7167.
- (11) Zheng, Z. , Hu, Q. , Zhang, S. , Zhang, D. , Wang, J. , Xie, S. , Wang, R. , Qin, Y. , Li, W. , Hong, L.; et al., (2018). A Highly Efficient Non-Fullerene Organic Solar Cell with a Fill Factor over 0.80 Enabled by a Fine-Tuned Hole-Transporting Layer. *Adv. Mater.* 30, 1801801.
- (12) Song, X. , Gasparini, N. , and Baran, D. (2017). The Influence of Solvent Additive on Polymer Solar Cells Employing Fullerene and Non-Fullerene Acceptors. *Adv. Electron. Mater.* 4, 1700358.
- (13) Song, X. , Gasparini, N. , Ye, L. , Yao, H. , Hou, J. , Ade, H. , and Baran, D. (2018). Controlling Blend Morphology for Ultrahigh Current Density in Nonfullerene Acceptor-Based Organic Solar Cells. *ACS Energy Lett.* 3, 669–676.
- (14) Nielsen, C. B., Holliday, S. , Chen, H.-Y. , Cryer, S. J. , and McCulloch, I. , (2015). Non-Fullerene Electron Acceptors for Use in Organic Solar Cells. *Acc. Chem. Res.* 48, 2803–2812.
- (15) Gasparini, N. , Lucera, L. , Salvador, M. , Prosa, M. , Spyropoulos, G. D. , Kubis, P. , Egelhaaf, H.-J. , Brabec, C. J. , and Ameri, T. , (2017). High-Performance Ternary Organic Solar Cells with Thick Active Layer Exceeding 11% Efficiency. *Energy Environ. Sci.* 10, 885–892.
- (16) Ameri, T. , Khoram, P. , Min, J. , and Brabec, C. J. , (2013). Organic Ternary Solar Cells: A Review. *Adv. Mater.* 25, 4245–4266.
- (17) Xiao, L. , He, B. , Hu, Q. , Maserati, L. , Zhao, Y. , Yang, B. , Kolaczkowski, M. A. ,

- Anderson, C. L. , Borys, N. J. , Klivansky, L. M.; et al ., (2018). Multiple Roles of a Non-Fullerene Acceptor Contribute Synergistically for High-Efficiency Ternary Organic Photovoltaics. *Joule* DOI: 10.1016/j.joule.2018.08.002.
- (18) Liu, T. , Luo, Z. , Fan, Q. , Zhang, G. , Zhang, L. , Gao, W. , Guo, X. , Ma, W. , Zhang, M. , Yang, C. , et al ., (2018). Use of Two Structurally Similar Small Molecular Acceptors Enabling Ternary Organic Solar Cells with High Efficiencies and Fill Factors. *Energy Environ. Sci.* 11, 3275–3282.
- (19) Zhang, H. , Yao, H. , Hou, J. , Zhu, J. , Zhang, J. , Li, W. , Yu, R. , Gao, B. , Zhang, S. , and Hou, J. (2018). Over 14% Efficiency in Organic Solar Cells Enabled by Chlorinated Nonfullerene Small-Molecule Acceptors. *Adv. Mater.* 30, 1800613.
- (20) Baran, D. , Ashraf, R. S. , Hanifi, D. A. , Abdelsamie, M. , Gasparini, N. , Röhr, J. A. , Holliday, S. , Wadsworth, A. , Lockett, S. , Neophytou, M. , et al., (2017). Reducing the Efficiency-Stability-Cost Gap of Organic Photovoltaics with Highly Efficient and Stable Small Molecule Acceptor Ternary Solar Cells. *Nat. Mater.* 16, 363–369.
- (21) Gasparini, N. , Jiao, X. , Heumueller, T. , Baran, D. , Matt, G. J. , Fladischer, S. , Spiecker, E. , Ade, H. , Brabec, C. J. , and Ameri, T. (2016). Designing Ternary Blend Bulk Heterojunction Solar Cells with Reduced Carrier Recombination and a Fill Factor of 77%. *Nat. Energy* 1, 118.
- (22) Lu, L. , Xu, T. , Chen, W. , Landry, E. S. , and Yu, L. , (2014). Ternary Blend Polymer Solar Cells with Enhanced Power Conversion Efficiency. *Nat. Photonics* 8, 716–722.
- (23) Wang, J.-L. , Yin, Q.-R. , Miao, J.-S. , Wu, Z. , Chang, Z.-F. , Cao, Y. , Zhang, R.-B. , Wang, J.-Y. , Wu, H.-B. , and Cao, Y. , (2015). Rational Design of Small Molecular Donor for Solution-Processed Organic Photovoltaics with 8.1% Efficiency and High Fill Factor via Multiple Fluorine Substituents and Thiophene Bridge. *Adv. Funct. Mater.* 25, 3514–3523.
- (24) Chen, Y. , Ye, P. , Jia, X. , Gu, W. , Xu, X. , Wu, X. , Wu, J. , Liu, F. , Zhu, Z.-G. ,

- Huang, H. , (2017). Tuning V_{oc} for High Performance Organic Ternary Solar Cells with Non-Fullerene Acceptor Alloys. *J. Mater. Chem. A* 8, 1704-1709.
- (25) Yan, J. , Liang, Q. , Liu, K. , Miao, J. , Chen, H. , Liu, S. , He, Z. , Wu, H. , Wang, J. , and Cao, Y. , (2017). Optimized Phase Separation and Reduced Geminate Recombination in High Fill Factor Small-Molecule Organic Solar Cells. *ACS Energy Lett.* 2, 14–21.
- (26) Zhao, F. , Li, Y. , Wang, Z. , Yang, Y. , Wang, Z. , He, G. , Zhang, J. , Jiang, L. , Wang, T. , Wei, Z. , et al., (2017). Combining Energy Transfer and Optimized Morphology for Highly Efficient Ternary Polymer Solar Cells. *Adv. Energy Mater.* 9, 1602552.
- (27) Babics, M. , Liang, R.-Z. , Wang, K. , Cruciani, F. , Kan, Z. , Wohlfahrt, M. , Tang, M.-C. , Laquai, F. , and Beaujuge, P. M. , (2018). Solvent Vapor Annealing-Mediated Crystallization Directs Charge Generation, Recombination and Extraction in BHJ Solar Cells. *Chem. Mater.* 30, 789–798.
- (28) Lee, J. , Ko, S.-J. , Seifrid, M. , Lee, H. , Luginbuhl, B. R. , Karki, A. , Ford, M. , Rosenthal, K. , Cho, K. , Nguyen, T.-Q. , et al., (2018). Bandgap Narrowing in Non-Fullerene Acceptors: Single Atom Substitution Leads to High Optoelectronic Response Beyond 1000 nm. *Adv. Energy Mater.* 8, 1801212.
- (29) Song, X. , Gasparini, N. , Nahid, M. M. , Chen, H. , Macphee, S. M. , Zhang, W. , Norman, V. , Zhu, C. , Bryant, D. , Ade, H. , et al., (2018). A Highly Crystalline Fused-Ring N-Type Small Molecule for Non-Fullerene Acceptor Based Organic Solar Cells and Field-Effect Transistors. *Adv. Funct. Mater.* 30, 1802895.
- (30) Liu, S. , Song, X. , Thomas, S. , Kan, Z. , Cruciani, F. , Laquai, F. , Bredas, J.-L. , and Beaujuge, P. M. , (2017). Thieno[3,4- c]Pyrrole-4,6-Dione-Based Polymer Acceptors for High Open-Circuit Voltage All-Polymer Solar Cells. *Adv. Energy Mater.* 7, 1602574.
- (31) Zhang, M. , Gao, W. , Zhang, F. , Mi, Y. , Wang, W. , An, Q. , Wang, J. , Ma, X. ,

- Miao, J. , Hu, Z. , et al., (2018). Efficient Ternary Non-Fullerene Polymer Solar Cells with PCE of 11.92% and FF of 76.5%. *Energy Environ. Sci.* 11, 841-849.
- (32) Liang, R.-Z. , Babics, M. , Savikhin, V. , Zhang, W. , Le Corre, V. M. , Lopatin, S. , Kan, Z. , Firdaus, Y. , Liu, S. , McCulloch, I. , et al., (2018). Carrier Transport and Recombination in Efficient “All-Small-Molecule” Solar Cells with the Nonfullerene Acceptor IDTBR. *Adv. Energy Mater.* 8, 1800264.
- (33) Ma, X. , Mi, Y. , Zhang, F. , An, Q. , Zhang, M. , Hu, Z. , Liu, X. , Zhang, J. , and Tang, W. , (2018). Efficient Ternary Polymer Solar Cells with Two Well-Compatible Donors and One Ultranarrow Bandgap Nonfullerene Acceptor. *Adv. Energy Mater.* 8, 1702854.
- (34) Zhao, W. , Li, S. , Zhang, S. , Liu, X. , and Hou, J. , (2017). Ternary Polymer Solar Cells Based on Two Acceptors and One Donor for Achieving 12.2% Efficiency. *Adv. Mater.* 29, 1604059.
- (35) Yu, R. , Zhang, S. , Yao, H. , Guo, B. , Li, S. , Zhang, H. , Zhang, M. , and Hou, J. , (2017). Two Well-Miscible Acceptors Work as One for Efficient Fullerene-Free Organic Solar Cells. *Adv. Mater.* 29, 1700437.
- (36) Zhang, G. , Zhang, K. , Yin, Q. , Jiang, X. F. , Wang, Z. , Xin, J. , Ma, W. , Yan, H. , Huang, F. , and Cao, Y. , (2017). High-Performance Ternary Organic Solar Cell Enabled by a Thick Active Layer Containing a Liquid Crystalline Small Molecule Donor. *J. Am. Chem. Soc.* 139, 2387–2395.
- (37) Koster, L. J. A. , Mihailetschi, V. D. , Ramaker, R. , and Blom, P. W. M. , (2005). Light Intensity Dependence of Open-Circuit Voltage of Polymer:fullerene Solar Cells. *Appl. Phys. Lett.* 86, 123509.
- (38) Cowan, S. R. , Roy, A. , and Heeger, A. J. , (2010). Recombination in Polymer-Fullerene Bulk Heterojunction Solar Cells. *Phys. Rev. B*, 82, 245207.
- (39) Li, S. , Ye, L. , Zhao, W. , Zhang, S. , Mukherjee, S. , Ade, H. , and Hou, J. ,

- (2016). Energy-Level Modulation of Small-Molecule Electron Acceptors to Achieve over 12% Efficiency in Polymer Solar Cells. *Adv. Mater.* 28, 9423–9429.
- (40) Zhong, L. , Gao, L. , Bin, H. , Hu, Q. , Zhang, Z. G. , Liu, F. , Russell, T. P. , Zhang, Z. , and Li, Y. (2017). High Efficiency Ternary Nonfullerene Polymer Solar Cells with Two Polymer Donors and an Organic Semiconductor Acceptor. *Adv. Energy Mater.* 7, 1602215.
- (41) Li, S. , Ye, L. , Zhao, W. , Yan, H. , Yang, B. , Liu, D. , Li, W. , Ade, H. , and Hou, J., (2018). A Wide Band Gap Polymer with a Deep Highest Occupied Molecular Orbital Level Enables 14.2% Efficiency in Polymer Solar Cells. *J. Am. Chem. Soc.* 140, 7159-7167.
- (42) Shuttle, C. G. , O'Regan, B. , Ballantyne, A. M. , Nelson, J. , Bradley, D. D. C. , de Mello, J. , and Durrant, J. R. , (2008). Experimental Determination of the Rate Law for Charge Carrier Decay in a Polythiophene: Fullerene Solar Cell. *Appl. Phys. Lett.* 92, 93311.
- (43) Stephen, M. , Genevičius, K. , Juška, G. , Arlauskas, K. , and Hiorns, R. C. , (2017). Charge Transport and Its Characterization Using Photo-CELIV in Bulk Heterojunction Solar Cells. *Polym. Int.* 66, 13–25.
- (44) Kniepert, J. , Schubert, M. , Blakesley, J. C. , and Neher, D. , (2011). Photogeneration and Recombination in P3HT/PCBM Solar Cells Probed by Time-Delayed Collection Field Experiments. *J. Phys. Chem. Lett.* 2, 700–705.
- (45) Gasparini, N. , Salvador, M. , Heumueller, T. , Richter, M. , Classen, A. , Shrestha, S. , Matt, G. J. , Holliday, S. , Strohm, S. , Egelhaaf, J. et al., (2017). Polymer:Nonfullerene Bulk Heterojunction Solar Cells with Exceptionally Low Recombination Rates. *Adv. Energy Mater.* 7, 1701561.
- (46) Hu, H. , Jiang, K. , Chow, P. C. Y. , Ye, L, Zhang, G. , Li, Z. , Carpenter, J. H. , Ade, H. , and Yan, H. , (2017). Influence of Donor Polymer on the Molecular Ordering of

- Small Molecular Acceptors in Nonfullerene Polymer Solar Cells. *Adv. Energy Mater.* 7, 1701674.
- (47) Collins, B. A. , Cochran, J. E. , Yan, H. , Gann, E. , Hub, C. , Fink, R. , Wang, C. , Schuettfort, T. , McNeill, C. R. , Chabinyk, M. L. , et al., (2012). Polarized X-Ray Scattering Reveals Non-Crystalline Orientational Ordering in Organic Films. *Nat. Mater.* 11, 536–543.
- (48) Tumbleston, J. R. , Collins, B. A. , Yang, L. , Stuart, A. C. , Gann, E. , Ma, W. , You, W. , and Ade, H. , (2014). The Influence of Molecular Orientation on Organic Bulk Heterojunction Solar Cells. *Nat. Photonics* 8, 385–391.
- (49) Zhao, J. , Li, Y. , Yang, G. , Jiang, K. , Lin, H. , Ade, H. , Ma, W. , and Yan, H. , (2016). Efficient Organic Solar Cells Processed from Hydrocarbon Solvents. *Nat. Energy.* 1, 15027.
- (50) Liu, Y. , Zhao, J. , Li, Z. , Mu, C. , Ma, W. , Hu, H. , Jiang, K. , Lin, H. , Ade, H. , and Yan, H. , (2014). Aggregation and Morphology Control Enables Multiple Cases of High-Efficiency Polymer Solar Cells. *Nat. Commun.* 5, 5293.
- (51) Mukherjee, S. , Jiao, X. , and Ade, H. , (2016). Charge Creation and Recombination in Multi-Length Scale Polymer:Fullerene BHJ Solar Cell Morphologies. *Adv. Energy Mater.* 6, 1600699.
- (52) Ran, N. A. , Love, J. A. , Heiber, M. C. , Jiao, X. , Hughes, M. P. , Karki, A. , Wang, M. , Brus, V. V. , Wang, H. , Neher, D. , et al., (2017). Charge Generation and Recombination in an Organic Solar Cell with Low Energetic Offsets. *Adv. Energy Mater.* 7, 1701073.
- (53) Rivnay, J. , Noriega, R. , Kline, R. J. , Salleo, A. , and Toney, M. F. , (2011). Quantitative Analysis of Lattice Disorder and Crystallite Size in Organic Semiconductor Thin Films. *Phys. Rev. B* 84, 045203.
- (54) Noriega, R. , Rivnay, J. , Vandewal, K. , Koch, F. P. V, Stingelin, N. , Smith, P. ,

- Toney, M. F. , and Salleo, A. , (2013). A General Relationship between Disorder, Aggregation and Charge Transport in Conjugated Polymers. *Nat. Mater.* 12, 1038–1044.
- (55) Cui, Y. , Yang, C. , Yao, H. , Zhu, J. , Wang, Y. , Jia, G. , Gao, F. , and Hou, J. (2017). Efficient Semitransparent Organic Solar Cells with Tunable Color Enabled by an Ultralow-Bandgap Nonfullerene Acceptor. *Adv. Mater.* 29, 1703080.

Figures – list of legends

Figure 1. a) Schematic of the inverted solar cell architecture used in this study. b) Chemical structures of the components forming the photoactive layer. c) Normalized absorbance profiles of the components depicted in (b).

Figure 2. a) Absorption coefficient for binary PTB7-Th:IEICO-4F and ternary PTB7-Th:BIT-4F-T:IEICO-4F blends with 10% and 20% BIT-4F-T addition b) Current density – voltage (J - V) characteristics at 1 sun equivalent illumination of the devices, c) External quantum efficiency (EQE) and integrated photocurrent measured for the corresponding devices in (b) and d) Δ EQE for 10% and 20% BIT-4F-T ternary blends with respect to the binary PTB7-Th:IEICO-4F device.

Figure 3. a) Current density-voltage (J - V) characteristics of the bilayer hole-only device based on ITO/PEDOT/BIT-4F-T/PTB7-Th/MoO_x/Ag; b) Open circuit voltage as a function of light intensity for the binary PTB7-Th:IEICO-4F, PTB7-Th:BIT-4F-T:IEICO-4F (10% BIT-4F-T) and PTB7-Th:BIT-4F-T:IEICO-4F (10% BIT-4F-T) devices; c) Photocurrent density vs effective voltage for the same devices depicted in b); d) charge extraction measurements for binary and ternary devices.

Figure 4. a-c) 2D Grazing incident wide-angle X-ray scattering, GIWAXS patterns of the 0, 10 and 20% BIT-4F-T samples, respectively; d) 1D GIWAXS line-cuts of the samples in the out of plane (OOP) direction (graphs are offset for clarity); e) OOP π - π stacking d-spacing and f) coherence length of PTB7-Th *versus* samples along with their respective device PCEs (blue spheres), showing an excellent agreement between the increased ordering and their PV performances.

Figure 5. The binary and ternary devices of PTB7-Th: PC₇₁BM system (b); the binary and ternary devices of PTB7-Th:IEICO system (c); the binary and ternary devices of PTB7-Th: IEICO-4Cl system (d).

Figure 6. Stability of 0% BIT-4F-T (binary) and 10% BIT-4F-T (ternary) devices. a, Photo-stability of binary and ternary solar cells (nitrogen atmosphere, under constant AM1.5G illumination at 1 sun, room temperature) for 500 hours. b, Shelf storage lifetime (dark, nitrogen atmosphere, room temperature) comparison of binary and ternary system for 20 days. c, Shelf storage lifetime (dark, 80 °C, nitrogen atmosphere) comparison of binary and ternary system for 20 days.