

Efficient Thick-Film Polymer Solar Cells with Enhanced Fill Factors via Increased Fullerene Loading

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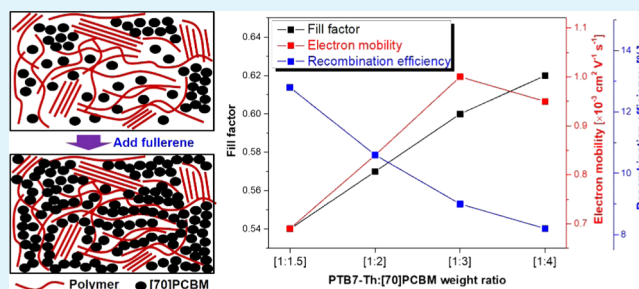
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Supporting Information

ABSTRACT: Developing effective methods to make efficient bulk-heterojunction polymer solar cells at roll-to-roll relevant active layer thickness is of significant importance. We investigate the effect of fullerene content in polymer:fullerene blends on the fill factor (FF) and on the performance of thick-film solar cells for four different donor polymers PTB7-Th, PDPP-TPT, BDT-FBT-2T, and poly[5,5'-bis(2-butyloctyl)-(2,2'-bithiophene)-4,4'-dicarboxylate-*alt*-5,5'-2,2'-bithiophene] (PDCBT). At a few hundreds of nanometers thickness, increased FFs are observed in all cases and improved overall device performances are obtained except for PDCBT upon increasing fullerene content in blend films. This fullerene content effect was studied in more detail by electrical and morphological characterization. The results suggest enhanced electron mobility and suppressed bimolecular recombination upon increasing fullerene content in thick polymer:fullerene blend films, which are the result of larger fullerene aggregates and improved interconnectivity of the fullerene phases that provide continuous percolating pathways for electron transport in thick films. These findings are important because an effective and straightforward method that enables fabricating efficient thick-film polymer solar cells is desirable for large-scale manufacturing via roll-to-roll processing and for multijunction devices.

KEYWORDS: polymer solar cells, thick films, fill factor, fullerene loading



INTRODUCTION

Polymer solar cells (PSCs) that employ a bulk heterojunction (BHJ) represent an interesting low-cost technology for future roll-to-roll production of flexible and large area photovoltaic modules via printing.^{1,2} Most often, the photoactive layer of a PSC is a physical blend of an electron-donating p-type conjugated polymer and an electron-accepting n-type conjugated small molecule. Benefitting from extensive research efforts that include developing novel conjugated polymer donors and acceptors, tuning the BHJ morphology, improvements in contacts, and device engineering, the power conversion efficiency (PCE) of PSCs now exceeds 15%.^{3,4} Stability studies revealed that an operational lifetime of up to 10 years can be achieved for PSCs, providing a promising prospect that PSCs can turn into a practically useful photovoltaic technology.^{5,6} However, most high-performing BHJ systems are very susceptible to the thickness of the photoactive layer. Generally, the optimal thickness is in a range

of 80–120 nm, which coincides with the first interference maximum of the optical electrical field in a layer stack with a reflective back electrode.^{7,8} Such thin films can be easily made in a laboratory but are more challenging to attain in high-speed and large-scale manufacturing where production yield is crucial.^{8–11} Moreover, the high susceptibility to thickness variations also limits the maximum attainable short-circuit current density (J_{sc}) and power conversion efficiencies (PCEs) of PSCs due to the fact that not all incident light is absorbed by an ~ 100 nm thick film.⁷

The main problem to be overcome with respect to film thickness is that PSCs usually show a sharp drop in the fill factor (FF) and J_{sc} upon increasing the thickness of the active layer.^{12,13} Such FF and J_{sc} drops are generally caused by poor

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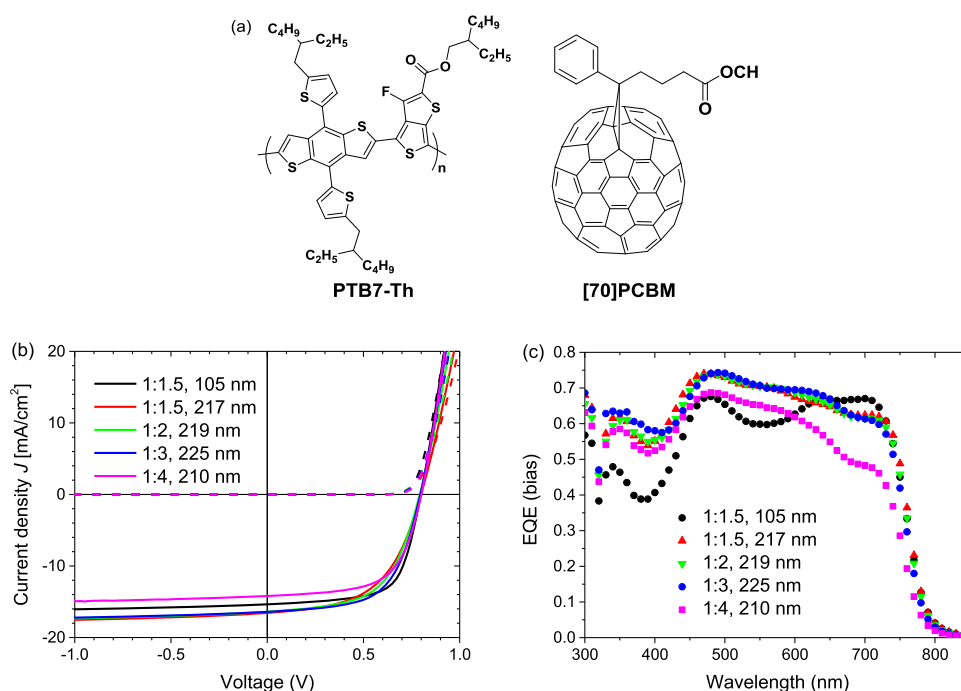


Figure 1. (a) Structures of PTB7-Th and [70]PCBM. (b) J - V characteristics of PTB7-Th:[70]PCBM solar cells under AM1.5G illumination (100 mW cm^{-2}). (c) Corresponding external quantum efficiency (EQE) spectra.

Table 1. Device Metrics of PTB7-Th:[70]PCBM Solar Cells with Various D/A Ratios

D/A	d (nm)	J_{sc} (mA cm^{-2})	V_{oc} (V)	FF	PCE (%)	R_s ($\Omega \text{ cm}^2$)	R_{sh} ($\Omega \text{ cm}^2$)
1:1.5	105	15.3	0.80	0.66	8.1	7.2	785
1:1.5	217	16.5	0.80	0.54	7.1	10.7	548
1:2	219	16.4	0.79	0.57	7.5	9.4	547
1:3	225	16.4	0.80	0.60	7.9	8.3	847
1:4	210	14.2	0.80	0.62	7.0	7.8	822

and imbalanced charge transport, which results in enhanced bimolecular charge recombination and the formation of space charge in thicker films.^{13–17} Considerable efforts have thus been devoted to improving the charge transport via rational material design^{12,13,18–24} and delicate morphology control.^{15,25–32} Developing a processing protocol for efficient thick-film PSCs that is applicable to a variety of conjugated polymers is of significant interest and importance.^{25–31} For example, Zhang et al. demonstrated that adding a nematic liquid crystalline small molecule (benzodithiophene terthiophene rhodamine) into thick active layers consisting of a blend of poly[4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b;4,5- b']dithiophene-2,6-diyl-*alt*-(4-(2-ethylhexyl)-3-fluorothieno[3,4- b']thiophene-)-2-carboxylate-2-6-diyl] (PTB7-Th) with [6,6]-phenyl- C_{71} -butyl acid methyl ester ([70]PCBM) (Figure 1a) can increase the hole mobility and PCE due to smaller π - π distance, longer coherence length, and improved domain purity of the donor phase.²⁷ On the other hand, a few studies have identified that the lack of a continuous channel for electron transport is a limiting factor when thickness increases.^{31,33–36} On the basis of this understanding, Huang et al.³¹ reported an inverted off-center spin-coating method that can improve the connectivity of the fullerene phase and electron transport in the vertical direction. In consequence, the PSCs show significantly improved device performance at large thickness.

A more versatile method to improve the connectivity of the acceptor phase is increasing the concentration of the fullerene acceptor in the polymer:fullerene blend.^{33–38} For example, Yin et al. observed that thin PSCs ($\sim 100 \text{ nm}$), which were optimized by the fill factor (FF), tended to have higher acceptor contents compared to the PSCs that were optimized by PCE.³⁶ Foster et al. demonstrated that the electron mobility and FF of $\sim 300 \text{ nm}$ thick-film PTB7:[6,6]-phenyl- C_{61} -butyl acid methyl ester ([60]PCBM) solar cells can be improved by increasing the content of [60]PCBM in the blend films.³⁵ Nevertheless, the PSCs in this report exhibited low PCEs and a decrease in PCE after increasing the fullerene content,³⁵ which obscures the real effect of fullerene loading on the performance of thick-film PSCs. Moreover, the enhancement of the FF in these reports was explained only by electrical characterization but no morphological information was given.^{35,36} Herein, we discuss how the electrical properties, morphology, and device performance of BHJ films at large layer thickness are affected by modulating the fullerene concentration. Specifically, a state-of-the-art conjugated polymer PTB7-Th³⁹ was used in combination with [70]PCBM to investigate the effect of fullerene loading on the performance of thick-film solar cells.

RESULTS AND DISCUSSION

PTB7-Th:[70]PCBM solar cells were fabricated with an optimal weight ratio of [1:1.5] at a layer thickness of ~ 100

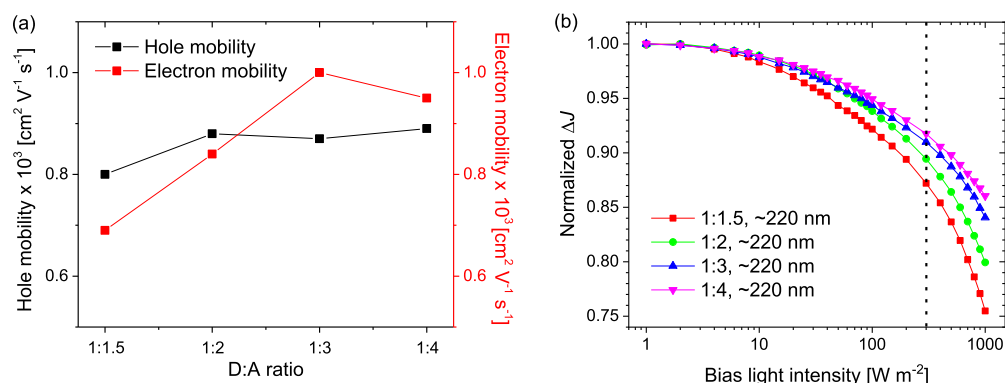


Figure 2. (a) Hole and electron mobility of thick PTB7-Th:[70]PCBM blend films (~ 220 nm) with various D/A ratios. (b) The differential current density of thick-film (~ 220 nm) solar cells of PTB7-Th:[70]PCBM with various D/A ratios as a function of light intensity. The vertical dotted line corresponds to the light intensity that affords the AM1.5G (100 mW cm^{-2}) photocurrent.

nm and for various other donor/acceptor weight ratios at a thickness of ~ 220 nm. The thickness for the thick devices was set to ~ 220 nm because this value is relevant to printing technologies and corresponds to the second interference maximum of the optical electrical field in PSC devices.⁷ The device layout used is indium tin oxide (ITO)/poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS)/PTB7-Th:[70]PCBM/LiF/Al. PTB7-Th and [70]PCBM were dissolved in different weight ratios in chlorobenzene using 3 vol % 1,8-diiodooctane as processing additive to form the casting solution. The current density–voltage (J – V) characteristics, measured under simulated AM1.5G (Air Mass 1.5 Global spectrum) illumination (100 mW cm^{-2}) conditions, are shown in Figure 1b. The external quantum efficiency (EQE) spectra of the cells are shown in Figure 1c, and the device metrics are collected in Table 1. The statistics of the device parameters are summarized in Table S1 (Supporting Information).

The optimal PTB7-Th:[70]PCBM solar cell with a weight ratio of [1:1.5] at a layer thickness of ~ 100 nm offered a PCE of 8.1% along with a FF of 0.66 and a J_{sc} of 15.3 mA cm^{-2} . Increasing the thickness to ~ 220 nm led to a drastically dropped PCE of 7.1%. This is because the FF sharply decreased to 0.54 although the J_{sc} increased slightly to 16.5 mA cm^{-2} . Meanwhile, the series resistance (R_{s}) increased whereas the shunt resistance (R_{sh}) decreased (Table 1). Interestingly, the FF of the thick-film solar cells increased monotonically from 0.54 to 0.62 when changing the weight ratio from [1:1.5] to [1:4]. Correspondingly, the R_{s} decreased monotonically whereas the R_{sh} increased monotonically (Table 1). The J_{sc} and EQE were almost unchanged for the [1:1.5], [1:2], and [1:3] devices at a thickness of ~ 220 nm. The [1:3] device afforded the highest PCE of 7.9%, which is considerably higher than that of the [1:1.5] device at the same ~ 220 nm active layer thickness. Moreover, this PCE value is equivalent to that of the optimal solar cells with the thin active layer. Notably, the [1:4] device that has a further increased fullerene content exhibited a substantially lower J_{sc} and EQE although the FF increased. Because the enhanced FF does not indicate a problem with charge extraction, the lower J_{sc} is likely due to reduced light absorption as a consequence of the fact that the content of the main absorber in the film has decreased at the [1:4] weight ratio (Figure S1 in the Supporting Information).

The effect of fullerene content on the performance of thick-film PTB7-Th cells was verified by employing [60]PCBM

instead of [70]PCBM as the electron acceptor. The J – V and EQE data are shown in Figure S2 (Supporting Information), and the device parameters are collected in Table S2 (Supporting Information). Increasing the [60]PCBM content in the PTB7-Th:[60]PCBM blends resulted in similar enhancements in FF and PCE for the [1:1.5] to [1:3] devices with an active layer thickness of ~ 200 nm. Moreover, solar cells with an inverted ITO/ZnO/PTB7-Th:[70]PCBM/MoO_x/Ag device architecture were fabricated and tested with various donor/acceptor ratios at large layer thickness. The device results are collected in Figure S3 and Table S3 in the Supporting Information. For the [1:1.5] devices, increasing the thickness from ~ 90 to ~ 200 nm led to a drastic decrease of the FF from 0.62 to 0.53. Along with increasing the content of [70]PCBM in the blend films, the FF increased gradually from 0.53 for the [1:1.5] device to 0.58 for the [1:3] device and further to 0.59 for the [1:4] device. Similar to the conventional device architecture, the [1:4] inverted device exhibited considerably reduced J_{sc} and EQE. The optimal balance between J_{sc} and FF was achieved for the [1:3] device, which produced the highest PCE of 7.8%, a value even higher than that of the optimal thin device. All in all, these results indicate that adjusting the fullerene concentration in PTB7-Th:[70]PCBM blend is a fruitful method to improve the performance of thick-film solar cells, independent of the structure of fullerene acceptor used and the device configuration.

To understand the effect of fullerene content on the FF and device performance of the thick-film solar cells based on PTB7-Th:[70]PCBM we investigated charge transport and recombination. The hole and electron mobilities were determined in single-carrier devices for different PTB7-Th:[70]PCBM blends by fitting the dark J – V data with a model for space charge limited current (Figure S4, Supporting Information). Figure 2a shows hole and electron mobilities of the PTB7-Th:[70]PCBM blends for various weight ratios at a film thickness of ~ 220 nm. For the [1:1.5] device, the electron mobility is lower than the hole mobility. Notably, this observation is different from the statement that the hole mobility is the limiting factor for the poor performance of thick-film PSCs.^{14,18} Going from the PTB7-Th:[70]PCBM ratio of [1:1.5] to [1:4], the hole mobility changes little. The electron mobility shows a clear increasing trend from [1:1.5] to [1:3] but decreases slightly when increasing the fullerene content further to a ratio of [1:4], in accordance with the FF and PCE

of the PTB7-Th:[70]PCBM solar cells. This trend is consistent with the results of Foster³⁵ observed in PTB7:[60]PCBM blends and of Yin³⁶ observed in PTB7:[70]PCBM blends with different fullerene content. A few studies have shown that the low electron mobility in polymer:fullerene BHJ films is due to a poor network of fullerene aggregates for electron transport.^{40–44} It has been reported that the coherence length derived from the fullerene diffraction peak is a good indication of the local ordering within [70]PCBM domains and controls the electron mobility.^{42,43} Increasing the fullerene content in PTB7-Th:[70]PCBM blends can improve the interconnectivity of fullerene phases and lead to the formation of continuous percolating pathways for electron transport.

A critical factor that often limits the FF of PSCs for thicker films is bimolecular recombination of charge carriers.^{45,46} Investigating the bimolecular recombination of the cells can provide insightful information on the dependence of the FF on the fullerene content of the PTB7-Th:[70]PCBM cells for thick films. Instead of measuring J_{sc} directly as a function of light intensity I , we measured the differential current density ΔJ caused by low-intensity modulated light ΔI , while increasing the total intensity I over three orders of magnitude.⁴⁷ This method is more sensitive in identifying bimolecular recombination losses than the conventional measurements of J_{sc} vs I . The differential current (ΔJ) was measured employing modulated monochromatic light (600 nm) of low intensity (ΔI) and lock-in detection, while simultaneously illuminating the solar cell with a 530 nm light from an light-emitting diode (LED) with increasing intensity. The bimolecular recombination efficiency (η_{BR}) at AM1.5G illumination condition can be estimated as $\eta_{BR} = 1 - \Delta J^{norm}$. The normalized ΔJ (ΔJ^{norm}) is shown in Figure 2b as a function of the total light intensity (average of LED and modulated monochromatic light) for PTB7-Th:[70]PCBM devices with a similar thickness of ~ 220 nm but different fullerene content. Under AM1.5G illumination, η_{BR} (at short circuit) amounts to 0.128, 0.106, 0.090, and 0.082 for the [1:1.5], [1:2], [1:3], and [1:4] weight ratios, respectively. These results clearly show that bimolecular recombination losses in PTB7-Th:[70]PCBM blend films are effectively suppressed upon increasing the content of fullerene acceptor, which thereby explains the FF trend of the solar cells.

The difference in photovoltaic, transport, and recombination characteristics can be related to changes in the nano-morphology of the PTB7-Th:[70]PCBM blends. The molecular packing of the polymer and fullerene in blend films was characterized by grazing incidence wide-angle X-ray scattering (GIWAXS).⁴⁸ The results for the thin (~ 100 nm) blend film with [1:1.5] ratio and thick (~ 220 nm) blend film with [1:1.5] and [1:3] ratios are shown in Figure 3a,b. The phase separation of the BHJ morphology was studied by resonant soft X-ray scattering (RSoXS)⁴⁹ and transmission electron microscopy (TEM). The results are shown in Figures 3c and 4a, respectively. Detailed film structure features are summarized in Tables S5 and S6 in the Supporting Information. When increasing the thickness from ~ 100 to ~ 220 nm for the [1:1.5] device, the coherence length of fullerene packing increased slightly from 1.96 to 2.06 nm, as determined from GIWAXS. Moreover, the thick PTB7-Th:[70]PCBM film shows a lower face-on/edge-on ratio. Such change in crystalline orientation is not uncommon when processing conditions differ.^{50,51} Similarly, the domain spacing resolved from RSoXS profiles decreased slightly from 25.4 to 24.8 nm. By increasing the

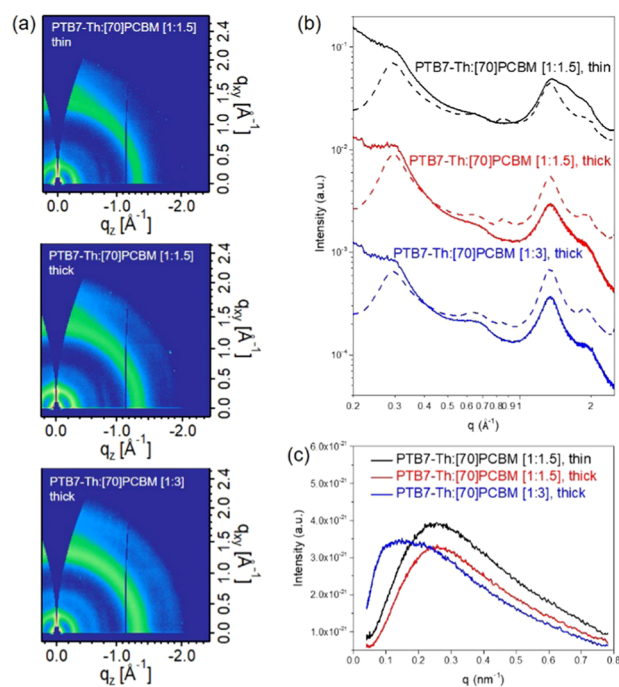


Figure 3. (a) Two-dimensional GIWAXS patterns of the blend films of PTB7-Th:[70]PCBM with specific D/A ratios and thickness, as indicated in the pictures. (b) Sector-averaged ($\pm 10^\circ$) profiles of the blend films (solid line: out-of-plane direction; dotted line: in-plane direction). (c) Lorentz corrected and thickness normalized RSoXS profiles of the blend films at the resonant energy of ~ 284 eV.

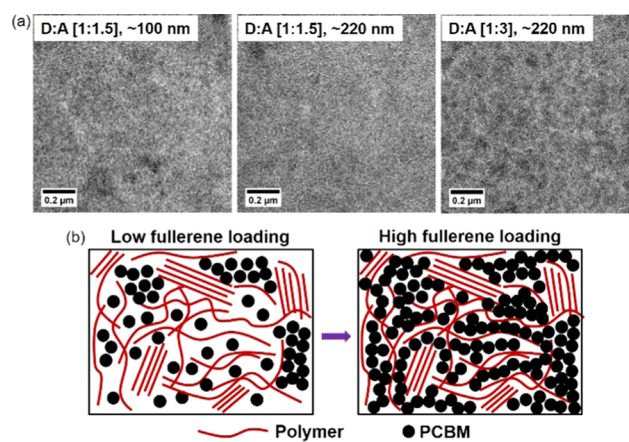


Figure 4. (a) Bright-field TEM images of PTB7-Th:[70]PCBM blend films. The D/A ratio and film thickness for each film are indicated. (b) Schematic of the thick PTB7-Th:[70]PCBM blend films with low and high fullerene content.

content of fullerene to a [1:3] ratio in the ~ 220 nm thick blend film, the fullerene coherence length increased further to 2.32 nm. This increased fullerene coherence length might be beneficial to improve the electron mobility.^{42–44} Additionally, the scattering intensity of the fullerene peak at $q \approx 0.7 \text{ \AA}^{-1}$, which has been linked to fullerene aggregation outside mixed domains,³³ increased for the thick film with higher [70]PCBM loading, suggesting that the [70]PCBM is vitrified in amorphous domains in the films with low [70]PCBM loading and phase-separated in the thick films with higher [70]PCBM content.⁵² These pure, aggregated [70]PCBM domains could provide electron-transporting pathways and thus improve the

device performance. More remarkably, the domain spacing increased significantly to 43.0 nm. TEM images shown in Figure 4a further verified these changes. For the [1:1.5] ratio, the thin (~100 nm) and thick (~220 nm) blend films show a rather homogeneous nanostructure with little contrast between PTB7-Th and [70]PCBM. Such a morphology that is too intermixed at low fullerene content hampers fast transport of photogenerated electrons due to long and tortuous percolation pathways, especially when the film thickness increases. After increasing the fullerene concentration, the [1:3] blend film shows a much less homogeneous film structure, which is indicative of distinct phase separation between PTB7-Th and [70]PCBM, consistent with the GIWAXS results discussed above. Increasing the fullerene content in blend films helps to form larger fullerene domains and to improve the interconnectivity of fullerene phases. Figure 4b shows a schematic description of the change in morphology upon increasing the fullerene content. As a consequence, the blend film exhibits higher electron mobility and less bimolecular charge recombination losses, which lead to a higher FF and overall device performance.

Having successfully improved the FF and overall performance of PTB7-Th:[70]PCBM-based thick-film solar cells by increasing the content of fullerene acceptor, we now test the general nature of this effect. Three donor polymers poly[2,5-bis(2-hexyldecyl)-2,3,5,6-tetrahydro-3,6-dioxopyrrolo[3,4-c]pyrrole-1,4-diyl]-*alt*-[2,2'-(1,4-phenylene)bisthiophene]-5,5'-diyl] (PDPP-TPT),⁵³ poly{(4,8-di(2,3-didecylthiophen-5-yl)benzo[1,2-*b*:4,5-*b'*]dithiophen-2,6-diyl)-*alt*-((4,7-di(thiophen-2-yl)-5,6-difluorobenzo[2,1,3]thiadiazole)-5,5'-diyl)} (BDT-FBT-2T),¹² and poly[5,5'-bis(2-butyloctyl)-(2,2'-bithiophene)-4,4'-dicarboxylate-*alt*-5,5'-2,2'-bithiophene] (PDCBT)⁵⁴ possessing distinct chemical structures (Figure S5 in the Supporting Information) were used in combination with [70]PCBM to fabricate thick-film solar cells. The $J-V$ characteristics and corresponding EQE spectra are shown in Figures S6–S8 (Supporting Information), respectively. The relevant device parameters and statistics are summarized in Tables S7–S9 (Supporting Information), respectively. When the thickness of blend films with the same D/A ratio optimized in thin films was increased, the resulting solar cells showed the expected decrease of FF for each polymer. For example, the FF of the BDT-FBT-2T-based device with the [1:1.5] ratio decreased from 0.70 for the ~100 nm device to 0.55 for the ~250 nm device. After increasing the fullerene content to a [1:3] ratio, the device with ~250 nm thickness produced an enhanced FF of 0.61. The solar cells of PDPP-TPT and BDT-FBT-2T also produced substantial J_{sc} when the fullerene content in blend films was changed, which thereby contributed to higher PCE in thick-film solar cells. A different behavior is observed for PDCBT:[70]PCBM blends, which also show an enhanced FF upon increasing fullerene content in thick films but in which the J_{sc} is very sensitive to the D/A ratio. As a result, the PCE of the solar cell with high fullerene content dropped drastically. Nanostructure characterizations of these blend films by GIWAXS and RSoXS offered results similar to those for PTB7-Th:[70]PCBM, i.e., increasing the fullerene content results in longer coherence length of fullerene packing and larger domain spacing. These results are presented in Figures S9–S11 and Tables S10 and S11 in the Supporting Information. Although the four polymers presented in this study afforded higher FFs for thick-film solar cells when increasing the fullerene content, further work is necessary to

establish as to what extent the effect is applicable to other donor polymers.

CONCLUSIONS

In conclusion, we have studied the effect of increasing fullerene content in polymer:fullerene blends on the FF and overall performance of thick-film bulk-heterojunction solar cells based on four different donor polymers. In all cases, enhanced fill factors are observed upon increasing fullerene content in blend films. Furthermore, an improved overall device performance is obtainable in thick-film devices for most donor polymers, suggesting the broad applicability of this approach. Electrical characterization verified that the improved FF and device performance result from enhanced electron mobility and suppressed bimolecular recombination. Further morphological investigation revealed that the higher fullerene content in blend films helps to form larger fullerene aggregates and to improve the interconnectivity of fullerene phases, providing continuous percolating pathways for electron transport in large film thickness. These findings are important because a simple and effective method that can enable efficient thick-film polymer solar cells is desirable for a variety of applications, such as roll-to-roll processing, and tandem devices. Moreover, a recent study showed that increasing the acceptor content can promote the FF also for nonfullerene PSCs with thin layers (~100 nm),³⁶ which suggests that the more in-depth investigations of the “acceptor-loading” effect on thick-film nonfullerene solar cells would be also very fruitful.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.9b00337.

Experimental details, $J-V$ curves of solar cells and single-carrier devices, GIWAXS patterns, RSoXS curves, device metrics of optimized ITO/PEDOT:PSS/PTB7-Th:[70]PCBM/LiF/Al solar cells, hole and electron mobilities of PTB7-Th:[70]PCBM films, structure features and characteristic length scale of phase separation (PDF)

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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