Efficient Organic Solar Cells with Polymer-Small Molecule: Fullerene Ternary Active Layers

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ABSTRACT: In this study, we report organic solar cells (OSCs) fabricated by a polymer-small molecule: the fullerene ternary active layer. It is found that a significantly enhanced power conversion efficiency contributed to the enhanced short-circuit current density and fill factor (FF). Investigation of absorption spectra and external quantum efficiency spectra indicate that the enhancement in photocurrent originates from the improved light absorption attributed to the small molecule. Further investigations by grazing-incidence wide-angle X-ray scattering, transmission electron microscopy, and atomic force microscopy reveal that charge transport within the ternary active layer is facilitated by a reduced σ-π distance between the adjacent polymer chains along the out-of-plane direction, good miscibilities between ternary components, and the rougher surface of the resultant thin film. As a result, the hole mobility of the polymer electron donor and electron mobility of the fullerene electron acceptor are considerably increased, resulting in enhanced FFs. Our studies provide a facile route to realize efficient OSCs.

1. INTRODUCTION
Organic solar cells (OSCs) are described as a promising approach for renewable energy generation and have gained intense attention due to their potential in large-area manufacturing by low-cost solution methods.1–3 Typically, OSCs are composed of polymers (or small molecules)/fullerene bulk heterojunction (BHJ) composite, where the BHJ composite as an active layer is sandwiched between the anode and cathode. To realize efficient OSCs, many stratagems have been employed.4–10 The key idea behind them is to take full advantage of the solar spectrum. Thus, two or more active layers are serially connected, and OSCs with multijunction structures are developed. Recently, over 11% PCEs from multijunction OSCs were realized.11,12 However, the fabrication and structure design of the multijunction OSCs are tricky.13,14 Alternatively, special efforts were paid to the structural modifications of polymers or small molecules to boost light harvest and charge generation. Over 10% PCEs from single-junction OSCs were reported.15–19 Nevertheless, light harvest by the thin active layer is limited by its thickness due to the trade-off correlation between charge generation and charge extraction.20–22 To circumvent these issues, the introduction of another electron donor material into the BHJ composite, possessing complimentary light absorption, was postulated and proved to be a facile approach.23–30 These BHJ composites based on three components were termed as a ternary active layer.

Efficient OSCs with a ternary active layer require complimentary light absorption between two electron donor materials. The added electron donor material has appropriate energy levels to function as a cascade for charge generation and transportation and good miscibilities between the ternary composites. Despite the simple concepts, optimization of the ternary active layer is difficult and complex,31 involving weight balance between the three components, solvent selections, and concentrations of processing additives.

In this study, we introduce a small molecule, 7,7′-(4,4-bis(2-ethylhexyl)-4H-silolo[3,2-b:4,5-b]-dithiophene-2,6-diyl)bis(6-fluoro-4-(5′-hexyl-[2,2′-bithiophen]-5-yl)benzo[c][1,2,5]-thiadiazole)32 (simplified as DTS) into poly[(4,8-bis(2-ethylhexyl)oxy]benzo[1,2-b:4,5-b′]dithiophene-2,6-diyl][3-fluoro-2-{(2-ethylhexyl)carbonyl}thieno[3,4-b]-thiophenediyl]- (PTB7)/[6,6]-phenyl-C71-butyric acid methyl ester (PC71BM) BHJ composite for fabricating OSCs. OSCs fabricated by the PTB7:DTS/PC71BM BHJ thin film exhibit a significantly enhanced short-circuit current ($J_{sc}$) and fill factor (FF), with a corresponding enhanced PCE of 8.88%, which is more than...
16% enhancement as compared to that (7.64%) of OSCs fabricated by the PTB7/PC71BM BHJ thin film. Investigation shows that DTS has complimentary light absorption with PTB7 in the visible range, and the photo-to-electron conversion efficiency within the OSCs with the ternary active layer is greatly increased. Further investigation indicates that the ternary components have a moderated phase separation and reduced \( \pi-\pi \) distance along the out-of-plane direction. Moreover, DTS not only improves the hole mobility of PTB7 and the electron mobility of PC71BM but also provides balanced charge carrier mobilities within the ternary active layer, leading to the enhanced FF. Our studies provide a facile route to realize efficient OSCs.

## 2. RESULTS AND DISCUSSION

To investigate the photovoltatic performances of OSCs based on the PTB7:DTS/PC71BM thin films, a series of active layers are employed, where the weight ratio of PTB7/PC71BM is kept at 1:1.5 and the weight content of DTS is tuned from 0 to 16.7 wt %. In addition, the volume ratio of the 1,8-diiodoctane (DIO) additive in chlorobenzene (CB) is tuned from 0.5 to 1 to 3% for optimizing the OSC photovoltaic performances. Figure 1a shows the current density versus voltage (J–V) characteristics of OSCs fabricated by PTB7/PC71BM, DTS/PC71BM, and the optimized PTB7:DTS/PC71BM thin films. The device performance parameters are summarized in Table 1.

### Table 1. Device Performance Parameters of OSCs Fabricated by the PTB7:DTS/PC71BM Thin Film under White Illumination (AM 1.5 G, 100 mW/cm²)

| PTB7:DTS/PC71BM (by weight) | DIO/CB (by volume) (%) | \( J_{SC} \) (mA cm\(^{-2}\)) | \( V_{OC} \) (V) | FF (%) | PCE (%) | \( R_s \) (\( \Omega \) cm\(^2\)) |
|-----------------------------|-----------------------|------------------|----------|-------|--------|----------------|
| 18:0:27                     | 3                     | 15.78            | 0.72     | 67.25 | 7.64   | 6.72           |
| 18:1:27                     | 17.22                 | 17.22            | 0.72     | 68.38 | 8.47   | 4.71           |
| 18:3:27                     | 17.28                 | 17.28            | 0.72     | 67.07 | 8.34   | 5.18           |
| 18:1:27                     | 16.91                 | 16.78            | 0.72     | 65.11 | 7.46   | 6.51           |
| 18:2:27                     | 16.79                 | 16.79            | 0.72     | 69.38 | 8.88   | 4.39           |
| 18:3:27                     | 16.68                 | 16.68            | 0.72     | 65.39 | 7.85   | 6.57           |
| 18:3:27                     | 16.69                 | 16.69            | 0.72     | 61.58 | 7.40   | 6.89           |
| 18:3:27                     | 16.98                 | 16.98            | 0.72     | 67.27 | 8.22   | 6.34           |
| 0:1:1                       | 11.63                 | 11.63            | 0.79     | 65.84 | 6.05   | 15.52          |

16% enhancement as compared to that (7.64%) of OSCs fabricated by the PTB7/PC71BM BHJ thin film. Investigation shows that DTS has complimentary light absorption with PTB7 in the visible range, and the photo-to-electron conversion efficiency within the OSCs with the ternary active layer is greatly increased. Further investigation indicates that the ternary components have a moderated phase separation and reduced \( \pi-\pi \) distance along the out-of-plane direction. Moreover, DTS not only improves the hole mobility of PTB7 and the electron mobility of PC71BM but also provides balanced charge carrier mobilities within the ternary active layer, leading to the enhanced FF. Our studies provide a facile route to realize efficient OSCs.

Figure 1. (a) J–V characteristics of OSCs under white illumination (AM 1.5 G, 100 mW/cm²) and (b) external quantum efficiency (EQE) spectra of OSCs.

### Table 1. Device Performance Parameters of OSCs Fabricated by the PTB7:DTS/PC71BM Thin Film under White Illumination (AM 1.5 G, 100 mW/cm²)

| PTB7:DTS/PC71BM (by weight) | DIO/CB (by volume) (%) | \( J_{SC} \) (mA cm\(^{-2}\)) | \( V_{OC} \) (V) | FF (%) | PCE (%) | \( R_s \) (\( \Omega \) cm\(^2\)) |
|-----------------------------|-----------------------|------------------|----------|-------|--------|----------------|
| 18:0:27                     | 3                     | 15.78            | 0.72     | 67.25 | 7.64   | 6.72           |
| 18:1:27                     | 17.22                 | 17.22            | 0.72     | 68.38 | 8.47   | 4.71           |
| 18:3:27                     | 17.28                 | 17.28            | 0.72     | 67.07 | 8.34   | 5.18           |
| 18:1:27                     | 15.91                 | 16.78            | 0.72     | 65.11 | 7.46   | 6.51           |
| 18:2:27                     | 16.79                 | 16.79            | 0.72     | 69.38 | 8.88   | 4.39           |
| 18:3:27                     | 16.68                 | 16.68            | 0.72     | 65.39 | 7.85   | 6.57           |
| 18:1:27                     | 16.69                 | 16.69            | 0.72     | 61.58 | 7.40   | 6.89           |
| 18:2:27                     | 16.98                 | 16.98            | 0.72     | 67.27 | 8.22   | 6.34           |
| 0:1:1                       | 11.63                 | 11.63            | 0.79     | 65.84 | 6.05   | 15.52          |
than 16% enhanced as compared to that of OSCs fabricated by the PTB7:PC71BM thin film. Moreover, it is also found that the greatly enhanced device performances mainly result from the significantly increased $J_{SC}$.

On the other hand, it is found that there is an apparent mutual compensation between DIO and DTS. Utilization of small amounts of DTS in PTB7:PC71BM could function as a substitution of DIO, as the PTB7:DTS:PC71BM thin film is
prepared from a CB solution with 0.5% DIO, and OSCs fabricated by the PTB7:DTS/PC71BM thin film with a weight ratio of 18:3:27 exhibit the best PCE; likewise, the best PCE is observed in OSCs fabricated by the PTB7:DTS/PC71BM (18:2:27) thin film, which is processed from a CB solution with 1% DIO. Whereas, the best PCE is observed in OSCs fabricated by the PTB7:DTS/PC71BM (18:1:27) thin film that is processed from a CB solution with 3% DIO.

According to the $J−V$ characteristics of OSCs, it is estimated that OSCs fabricated by the PTB7:DTS/PC71BM thin film only possess a low series resistance ($R_S$) of 4.39 Ω cm$^2$; in contrast, OSCs fabricated by the PTB7/PC71BM thin film possess a higher $R_S$ of 6.72 Ω cm$^2$. These results indicate that the improved $J_{SC}$ contributes to the reduced resistance of the devices. Thus, the introduction of the small molecule DTS into the PTB7/PC71BM binary active layer would greatly improve the PCEs of OSCs.

To study the strikingly increased $J_{SC}$ and improved PCE, the EQE spectra of the OSCs fabricated by the PTB7/PC71BM thin film and PTB7:DTS/PC71BM thin film are measured. The results are displayed in Figure 1b. Both OSCs have strong and broad responses in wavelengths ranging from 360 to 740 nm. Besides, it is observed that the OSCs fabricated by the PTB7:DTS/PC71BM thin film have enhanced EQE responses ranging from 350 to 700 nm as compared with those of the OSCs fabricated by the PTB7/PC71BM thin film. These results suggest that the improved $J_{SC}$ and PCE of the OSCs fabricated by the PTB7:DTS/PC71BM thin film are originated from the improved photo-to-electron conversions in the visible range, which probably contributes to the charge carrier generation and transportation within DTS. To confirm this, the band alignment of the materials used for fabrication of the OSCs by the PTB7:DTS/PC71BM thin film is shown in Scheme 1b. The highest occupied molecular orbital and lowest unoccupied molecular orbital energy levels of DTS are $−3.3$ and $−5.2$ eV, respectively, which are between the corresponding energy levels ($−3.3$ and $−5.1$ eV) of PTB7 and those of PC71BM, respectively. Therefore, DTS will not only work as an electron donor but also as a cascade in the energy level alignment.

To further investigate the improved $J_{SC}$ of the OSCs fabricated by the PTB7:DTS/PC71BM thin film, UV–visible absorption spectra of the PTB7, PC71BM, DTS, PTB7/PC71BM, DTS/PC71BM, and PTB7:DTS/PC71BM thin films are measured and the results are shown in Figure 2. Both PTB7

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**Figure 3.** Tapping-mode AFM height images of (a) PTB7/PC71BM thin film and (c) PTB7:DTS/PC71BM thin film; phase images of (b) PTB7/PC71BM thin film and (d) PTB7:DTS/PC71BM thin film.
and DTS possess strong light absorption ranging from 500 to 700 nm because they possess high molar extinction coefficients. However, the DTS thin film presents an overwhelming light absorption ranging from 320 to 460 nm as compared to that from the PTB7 thin film. Therefore, DTS can work complimentary to PTB7 for light absorption as it is compared to that from the PTB7 thin film. These results further indicate that the greatly enhanced EQE are attributed to the increased light absorption of the PTB7:DTS/PC71BM thin film. It is observed that introducing DTS into the PTB7/PC71BM thin film does not give rise to significant changes in the phase separation, which suggests that there is a good miscibility between DTS, PTB7, and PC71BM. As a result, the PTB7:DTS/PC71BM thin film possesses a good interpenetrating network, with a characteristic size scale of ~10 nm. The characteristic size scale within this range is favorable for high exciton dissociation efficiency, thus leading to an optimized device performance.

The two-dimensional (2D) grazing-incidence wide-angle X-ray scattering (GIWAXS) patterns of the PTB7/PC71BM and PTB7:DTS/PC71BM thin films are shown in Figure 5a,b. It is obvious that the addition of DTS affects the molecular packing of the PTB7 thin film. Figure 5c,d presents the one-dimensional (1D) GIWAXS patterns of the thin films along the in-plane direction ($q_x$) and out-of-plane direction ($q_y$). The different positions of the Bragg peaks along the in-plane direction ($q_x$) and out-of-plane direction ($q_y$) suggest isotropic packing stratagems of the polymer chains. From the position of the Bragg peak, the distance between adjacent PTB7 units along the π-π conjugation direction can be estimated. The structural parameters of thin films are summarized in Table 2. It is further found that an addition of DTS has impressive impacts on the molecular packing of the PTB7 thin film. The π-π distance along the in-plane direction is reduced from 4.80 to 4.72 Å. Moreover, the π-π distance along the out-of-plane direction is considerably reduced from 4.72 to 4.59 Å. It is noted that the photocurrent generated in OSCs is transported along the out-of-plane direction. Therefore, the greatly reduced π-π distance along the out-of-plane direction would facilitate the charge transport properties of the active layer. Thus, significantly improved $J_{SC}$ and FF are obtained from OSCs fabricated by the PTB7:DTS/PC71BM thin film.

To further study the influences of DTS on $J_{SC}$ and PCE of OSCs, the hole mobility of PTB7 and electron mobility of PC71BM in the active layers estimated on the basis of the space-charge-limited current (SCLC) method, followed the Mott–Gurney square law: $J = \frac{9}{8}\varepsilon_0\varepsilon_r\frac{V^2}{L^2}$, where $\varepsilon_0$ is the permittivity of free space, $\varepsilon_r$ is the dielectric constant of the polymer, which is assumed as 3, $L$ is the thickness of the active layer, $\mu$ is the carrier mobility. Figure 6 shows the $J^{1/2}$–$V$ curves of the hole-only diode, with a device structure of ITO/PEDOT:PSS/active layer/MoO3/Al, and the electron-only diode, with a device structure of ITO/Al/active layer/CA/Al, where the active layers are PTB7/PC71BM, DTS/PC71BM, and PTB7:DTS/PC71BM thin films. The hole mobility of PTB7 within the PTB7/PC71BM thin film is estimated to be 3.94 × 10^{-5} cm^2 V^{-1} s^{-1} and the electron mobility of PC71BM within the PTB7/PC71BM thin film is estimated to be 1.25 × 10^{-4} cm^2 s^{-1}.
V^{-1} s^{-1}, respectively, as given in Table 3. As DTS is introduced into the PTB7/PC_{71}BM thin film, the hole mobility of PTB7 is estimated to be to 5.57 \times 10^{-3} cm^2 V^{-1} s^{-1} and the electron mobility of PC_{71}BM is estimated to be 1.83 \times 10^{-4} cm^2 V^{-1} s^{-1}, respectively. It is also found that the ratio of the hole mobility to the electron mobility is decreased from 31.5 for the PTB7/PC_{71}BM thin film to 30.4 for the PTB7:DTS/PC_{71}BM thin film. Thus, an addition of DTS also can slightly balance the hole mobility of PTB7 and the electron mobility of PC_{71}BM. As a result, a weak enlarged FF is observed from OSCs fabricated by the PTB7:DTS/PC_{71}BM thin film.

### Table 2. Structural Parameters of PTB7/PC_{71}BM and PTB7:DTS/PC_{71}BM Thin Films

| Thin Film    | $q_y$ (Å^{-1}) | $\pi-\pi$ Distance (in-plane) (Å) | $q_z$ (Å^{-1}) | $\pi-\pi$ Distance (out-of-plane) (Å) |
|--------------|----------------|----------------------------------|----------------|-------------------------------------|
| PTB7/PC_{71}BM | 1.31           | 4.80                             | 1.33           | 4.72                                |
| PTB7:DTS/PC_{71}BM | 1.33           | 4.72                             | 1.37           | 4.59                                |

3. CONCLUSIONS

In summary, we demonstrated that the OSCs fabricated by the PTB7:DTS/PC_{71}BM thin film exhibit a significantly enhanced PCE of 8.88%. It was found that the greatly increased PCE contributed to the enhanced $J_{SC}$ and FF. Investigation of absorption spectra and EQE spectra indicated that the enhancement in $J_{SC}$ was originated from the improved light absorption. Further, investigations by GIWAXS, TEM, and AFM demonstrated that the charge transport within the PTB7:DTS/PC_{71}BM thin film was facilitated due to the
charge carrier mobilities and consequently an enlarged FF. Our studies provided a facile route to realize efficient OSCs.

4. EXPERIMENTAL SECTION

4.1. Materials. PTB7, PC71BM, and DTS were purchased from 1-Material Inc. and used as received. Poly[(9,9-bis(3′- (N,N-dimethylamino)propyl)-2,7-fluorene)-alt-2,7-(9,9-dioctylfluorene)] (PFN) was synthesized in our lab. The molecular structures of PTB7, DTS, PC71BM, and PFN are shown in Scheme 1. The poly(3,4-ethylenedioxythiophene):poly-(styrenesulfonate) PEDOT:PSS (Clevios HTL Solar) was purchased from Heraeus and used as received.

4.2. Thin-Film Characterizations. The PTB7, DTS, PC71BM, and their composite thin films were spin cast from CB with 1% v/v DIO solutions onto quartz glass. The thickness of the thin film is measured by the surface profilometer (Tencor, α-500). UV–vis absorption spectra of thin films were measured by an HP8453 spectrophotometer. The GIWAXS patterns of the PTB7/PC71BM and PTB7:DTS/PC71BM thin films were measured in a beamline 8-ID-E, Advanced Photon Source, Argonne National Laboratory. TEM images of the PTB7/PC71BM and PTB7:DTS/PC71BM thin films were captured by a JEOL TEM using an accelerating voltage of 120 kV. AFM images of the PTB7/PC71BM and the PTB7:DTS/PC71BM thin films were taken on a Nanoscope NS3A system (Digital Instrument).

4.3. Mobility Measurement. The SCLC method used to estimate the hole mobility of PTB7 within the PTB7/PC71BM and PTB7:DTS/PC71BM thin films and the electron mobility of PC71BM within the PTB7/PC71BM and PTB7:DTS/PC71BM thin films, followed the Mott–Gurney square law:

\[
\frac{J}{V^{1/2}} = \frac{9}{4\varepsilon r_{0}^{2}} \varepsilon_{0} \mu \frac{L}{t},
\]

where \(\varepsilon\) is the permittivity of free space, \(r_{0}\) is the dielectric constant of the polymer, which is assumed as 3, \(L\) is the thickness of active layer, \(\mu\) is the carrier mobility. The hole-only diode with a device structure of ITO/PEDOT:PSS/active layer/MoO3/Al and the electron-only diode with a device structure of ITO/Al/active layer/Ca/Al were fabricated, respectively, where ITO is indium tin oxide, the active layers are the PTB7/PC71BM and PTB7:DTS/PC71BM thin films, MoO3 is molybdenum oxide, Ca is calcium and Al is aluminum. The active layers were deposited using the same method as that for OSC fabrication. Ca with a thickness of 10 nm and Al with a thickness of 90 nm were deposited onto the active layers in the vacuum system with a base pressure of 2.0 × 10⁻³ mbar through a shadow mask. The active area of the device is measured to be 16 mm².

4.4. OSCs Fabrication and Characterizations. OSCs with a device structure of ITO/PEDOT:PSS/active layer/PFN/Al (as shown in Scheme 1a) were fabricated and characterized. The ITO substrates were cleaned in an ultrasonic bath with acetone, detergent, de-ionized water, and isopropanol, subsequently. After being dried in an oven overnight, the pre-cleaned ITO substrates were treated in a UV-ozone incubator. Then, PEDOT:PSS thin films with a thickness of around 40 nm were deposited atop the ITO substrates, followed by thermal annealing at 150 °C for 15 min. The active layers of the PTB7:DTS/PC71BM and PTB7:DTS/PC71BM thin films were deposited atop the PEDOT:PSS thin film from corresponding solutions (where CB mixed with DIO was used as the co-solvent, and the volume ratio of DIO was adjustable). After the active layers were dried for over 5 h at room temperature under vacuum, an ultrathin film of PFN with a

reduced \(\pi-\pi\) distance between the adjacent polymer chains along the out-of-plane direction and good miscibility of DTS in the composite. As a result, an enlarged \(J_{SC}\) is observed from the OSCs fabricated by the PTB7:DTS/PC71BM thin film. Moreover, the hole mobility of PTB7 and electron mobility of PC71BM were considerably increased, resulting in balanced

![Figure 6. \(J^{1/2}-V\) plots of the (a) hole-only device and (b) electron-only device, fabricated by PTB7/PC71BM, DTS/PC71BM, and PTB7:DTS/PC71BM thin films.](image-url)

| Table 3. Hole Mobility (\(\mu_{h}\)) of PTB7 and Electron Mobility (\(\mu_{e}\)) of PC71BM in the PTB7/PC71BM and PTB7:DTS/PC71BM Thin Films |
|-----|-----|-----|-----|
| active layer | \(\mu_{h}\) (cm² V⁻¹ s⁻¹) | \(\mu_{e}\) (cm² V⁻¹ s⁻¹) | \(\mu_{h}/\mu_{e}\) |
| PTB7/PC71BM | 3.94 × 10⁻³ | 1.25 × 10⁻⁴ | 31.5 |
| PTB7:DTS/PC71BM | 5.57 × 10⁻⁴ | 1.83 × 10⁻⁴ | 30.4 |
thickness of ~5 nm was spin cast onto the top of the active layers from its corresponding solution. Finally, 100 nm of Al was thermally deposited through a shadow mask in a vacuum chamber with a base pressure of 2.0 × 10^{-6} mbar. The active area of the device is measured to be 16 mm².

The current density versus voltage (J-V) characteristics of OSCs were measured by a Keithley 2400 source meter under AM 1.5 G spectrum from a class solar simulator (SAN-EI, XES-40S1, Japan) with the light intensity of 100 mW/cm². The light intensity was calibrated by a Newport-certified reference silicon cell (PV Measurements, with KG-5 visible filter). A spectral mismatch factor (M) value of 1.03 was used to obtain real photocurrents and efficiencies of the devices according to the previous report.49 The thicknesses of the active layers were prepared through a shadow mask in a vacuum area of the device is measured to be 16 mm².

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The authors declare no competing financial interest.

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■ REFERENCES

(1) Li, G.; Shrotriya, V.; Huang, J.; Yao, Y.; Moriarty, T.; Emery, K.; Yang, Y. High-efficiency solution processable polymer photovoltaic cells by self-organization of polymer blends. Nat. Mater. 2005, 4, 864–868.

(2) Zhao, G.; He, Y.; Li, Y. 6.5% Efficiency of polymer solar cells based on poly(3-hexylthiophene) and indene-C(60) bisadduct by device optimization. Adv. Mater. 2010, 22, 4355–4358.

(3) Kaltenbrunner, M.; White, M. S.; Glowacki, E. D.; Sekitani, T.; Someya, T.; Sariciftci, N. S.; Bauer, S. Ultrathin and lightweight organic solar cells with high flexibility. Nat. Commun. 2012, 3, No. 770.

(4) Chen, J.; Cao, Y. Development of Novel Conjugated Donor Polymers for High-Efficiency Bulk-Heterojunction Photovoltaic Devices. Acc. Chem. Res. 2009, 42, 1709–1718.

(5) Lin, Y.; Li, Y. F.; Zhan, X. W. Small molecule semiconductors for high-efficiency organic photovoltaics. Chem. Soc. Rev. 2012, 41, 4245–4272.

(6) Troshin, P. A.; Hoppe, H.; Rens, J.; Egingger, M.; Mayorova, J. Y.; Goryachev, A. E.; Peregudov, A. S.; Lyubovskaya, R. N.; Gobsch, G.; Sariciftci, N. S.; Razumov, V. F. Material Solubility-Photovoltaic Performance Relationship in the Design of Novel Fullerene Derivatives for Bulk Heterojunction Solar Cells. Adv. Funct. Mater. 2009, 19, 779–788.

(7) Ameri, T.; Dennler, G.; Lungenschmied, C.; Brabec, C. J. Organic tandem solar cells: A review. Energy Environ. Sci. 2009, 2, 347–363.

(8) Yaacobi-Gross, N.; Treat, N. D.; Pattanasattayavong, P.; Faber, H.; Perumal, A. K.; Stingelin, N.; Bradley, D. C. J.; Stavrinou, P. N.; Heeney, M.; Anthopoulos, T. D. High-Efficiency Organic Photovoltaic Cells Based on the Solution-Processable Hole Transporting Interlayer Copper Thiooctanoate (CuSCN) as a Replacement for PEDOT:PSS. Adv. Energy Mater. 2015, 5, No. 1501529.

(9) Yip, H.-L.; Jen, A. K. Y. Recent advances in solution-processed interfacial materials for efficient and stable polymer solar cells. Energy Environ. Sci. 2012, 5, 5994–6011.

(10) Li, Y. Molecular design of photovoltaic materials for polymer solar cells: toward suitable electronic energy levels and broad absorption. Acc. Chem. Res. 2012, 45, 723–733.

(11) Chen, C. C.; Chang, W. H.; Yoshimura, K.; Ohya, K.; You, J.; Gao, J.; Hong, Z.; Yang, Y. An efficient triple-junction polymer solar cell having a power conversion efficiency exceeding 11%. Adv. Mater. 2014, 26, 5670–5677.

(12) Yusoff, A. B.; Kim, D.; Kim, H. P.; Shneider, F. K.; da Silva, W. J.; Jang, J. A high efficiency solution processed polymer inverted triple-junction solar cell exhibiting a power conversion efficiency of 11.83%. Energy Environ. Sci. 2015, 8, 303–316.

(13) Siddiki, M. K.; Li, J.; Galipeau, D.; Qiao, Q. A review of polymer multijunction solar cells. Energy Environ. Sci. 2010, 3, 867–883.

(14) You, J.; Dou, L.; Hong, Z.; Li, G.; Yang, Y. Recent trends in polymer tandem solar cells research. Prog. Polym. Sci. 2013, 38, 1909–1928.

(15) Hu, H.; Jiang, K.; Yang, G.; Liu, J.; Li, Z.; Lin, H.; Liu, Y.; Zhao, J.; Zhang, J.; Huang, F.; Qu, Y.; Ma, W.; Yan, H. Terthiophene-Based D–A Polymer with an Asymmetric Arrangement of Alkyl Chains That Enables Efficient Polymer Solar Cells. J. Am. Chem. Soc. 2015, 137, 14149–14157.

(16) Liu, C.; Yi, C.; Wang, K.; Yang, Y.; Bhatia, R. S.; Tsige, M.; Xiao, S.; Gong, X. Single-Junction Polymer Solar Cells with Over 10% Efficiency by a Novel Two-Dimensional Donor–Acceptor Conjugated Copolymer. ACS Appl. Mater. Interfaces 2015, 7, 4928–4935.

(17) Yao, Z.; Zhang, M.; Wu, H.; Yang, L.; Li, R.; Wang, P. Donor/ Acceptor Indenopyrrole Dye for Highly Efficient Organic Dye-Sensitized Solar Cells. J. Am. Chem. Soc. 2015, 137, 3799–3802.

(18) Yang, Y.; Zhang, Z. G.; Bin, H.; Chen, S.; Gao, L.; Xue, L.; Yang, C.; Li, Y. Side-Chain Isomerization on an n-type Organic Semiconductor ITIC Acceptor Makes 11.77% High Efficiency Polymer Solar Cells. J. Am. Chem. Soc. 2016, 138, 15011–15018.

(19) Bin, H.; Gao, L.; Zhang, Z. G.; Yang, Y.; Zhang, Y.; Zhang, C.; Chen, S.; Xue, L.; Yang, C.; Xiao, M.; Li, Y. 11.4% Efficiency non-fullerene polymer solar cells with trialkylsilyl substituted 2D-conjugated polymer as donor. Nat. Commun. 2016, 7, No. 13651.

(20) Lenes, M.; Koster, L. J. A.; Mihailetschi, V. D.; Blom, P. W. M. Thickness dependence of the efficiency of polymer/fullerene bulk heterojunction solar cells. Appl. Phys. Lett. 2006, 88, No. 243502.

(21) Kirchartz, T.; Agostinelli, T.; Campoy-Quiles, M.; Gong, W.; Nelson, J. Understanding the Thickness-Dependent Performance of Organic Bulk Heterojunction Solar Cells: The Influence of Mobility, Lifetime, and Space Charge. J. Phys. Chem. Lett. 2012, 3, 3470–3475.

(22) Blom, P. W. M.; Mihailetschi, V. D.; Koster, L. J. A.; Markov, D. E. Device Physics of Polymer:Fullerene Bulk Heterojunction Solar Cells. Adv. Mater. 2007, 19, 1551–1566.

(23) An, Q.; Zhang, F.; Zhang, J.; Tang, W.; Deng, Z.; Hu, B. Versatile ternary organic solar cells: a critical review. Energy Environ. Sci. 2016, 9, 281–322.

(24) Liu, T.; Huo, L.; Sun, X.; Fan, B.; Cai, Y.; Kim, T.; Kim, J. Y.; Choi, H.; Sun, Y. Ternary Organic Solar Cells Based on Two Highly Efficient Polymer Donors with Enhanced Power Conversion Efficiency. Adv. Energy Mater. 2016, 6, No. 1502109.

(25) Lin, R.; Wright, M.; Purden Veettil, B.; Uddin, A. Enhancement of ternary blend organic solar cell efficiency using PTB7 as a sensitizer. Synth. Met. 2014, 192, 113–118.

(26) Cheng, P.; Zhan, X. Versatile third components for efficient and stable organic solar cells. Mater. Horiz. 2015, 2, 462–485.
(27) Cheng, P.; Zhang, M.; Lau, T. K.; Wu, Y.; Jia, B.; Wang, J.; Yan, C.; Qin, M.; Lu, X.; Zhan, X. Realizing Small Energy Loss of 0.55 eV, High Open-Circuit Voltage >1 V and High Efficiency >10% in Fullerene-Free Polymer Solar Cells via Energy Driver. Adv. Mater. 2017, 29, No. 1605216.

(28) Cheng, P.; Yan, C.; Wu, Y.; Wang, J.; Qin, M.; An, Q.; Cao, J.; Luo, L.; Zhang, F.; Ding, L.; Sun, Y.; Ma, W.; Zhan, X. Alloy Acceptors: Superior Alternative to PCBM toward Efficient and Stable Organic Solar Cells. Adv. Mater. 2016, 28, 8021–8028.

(29) Cheng, P.; Yan, C.; Lau, T. K.; Mai, J.; Lu, X.; Zhan, X. Molecular Lock: A Versatile Key to Enhance Efficiency and Stability of Organic Solar Cells. Adv. Mater. 2016, 28, 5822–5829.

(30) Cheng, P.; Ye, L.; Zhao, X.; Hou, J.; Li, Y.; Zhan, X. Binary additives synergistically boost the efficiency of all-polymer solar cells up to 3.45%. Energy Environ. Sci. 2014, 7, 1351–1356.

(31) Huang, J.-H.; Velusamy, M.; Ho, K.-C.; Lin, J.-T.; Chu, C.-W. A ternary cascade structure enhances the efficiency of polymer solar cells. J. Mater. Chem. 2010, 20, 2820.

(32) van der Poll, T. S.; Love, J. A.; Nguyen, T.-Q.; Bazan, G. C. Non-Basic High-Performance Molecules for Solution-Processed Organic Solar Cells. Adv. Mater. 2012, 24, 3646–3649.

(33) Liang, Y.; Xu, Z.; Xia, J.; Tsai, S. T.; Wu, Y.; Li, G.; Ray, C.; Yu, L. For the bright future-bulk heterojunction polymer solar cells with power conversion efficiency of 7.4%. Adv. Mater. 2010, 22, E135–E138.

(34) van der Poll, T. S.; Love, J. A.; Nguyen, T. Q.; Bazan, G. C. Non-basic high-performance molecules for solution-processed organic solar cells. Adv. Mater. 2012, 24, 3646–3649.

(35) Ohori, Y.; Fujii, S.; Kataura, H.; Nishio, Y. Improvement of bulk heterojunction organic solar cells based on PTB7-PC61BM with small amounts of P3HT. Jpn. J. Appl. Phys. 2014, 53, No. 04DK09.

(36) Zhou, E.; Cong, J.; Hashimoto, K.; Tajima, K. Control of Miscibility and Aggregation Via the Material Design and Coating Process for High-Performance Polymer Blend Solar Cells. Adv. Mater. 2013, 25, 6991–6996.

(37) Li, Z.; Lin, J. D.; Phan, H.; Sharenko, A.; Proctor, C. M.; Zalar, P.; Chen, Z.; Facchetti, A.; Nguyen, T. Q. Competitive Absorption and Inefficient Exciton Harvesting: Lessons Learned from Bulk Heterojunction Organic Photovoltaics Utilizing the Polymer Acceptor P (NDI2OD-T2). Adv. Funct. Mater. 2014, 24, 6989–6998.

(38) Miao, J.; Chen, H.; Liu, F.; Zhao, B.; Hu, L.; He, Z.; Wu, H. Efficiency enhancement in solution-processed organic small molecule: Fullerene solar cells via solvent vapor annealing. Appl. Phys. Lett. 2015, 106, No. 183302.

(39) Liu, F.; Gu, Y.; Jung, J. W.; Jo, W. H.; Russell, T. P. On the morphology of polymer-based photovoltaics. J. Polym. Sci., Part B: Polym. Phys. 2012, 50, 1018–1044.

(40) Dang, M. T.; Hirsch, L.; Wantz, G.; Wuest, J. D. Controlling the morphology and performance of bulk heterojunctions in solar cells. Lessons learned from the benchmark poly(3-hexylthiophene):[6,6]-phenyl-C61-butyric acid methyl ester system. Chem. Rev. 2013, 113, 3734–3765.

(41) Ye, L.; Zhang, S.; Ma, W.; Fan, B.; Guo, X.; Huang, Y.; Ade, H.; Hou, J. From binary to ternary solvent: morphology fine-tuning of D/A blends in PDPP3T-based polymer solar cells. Adv. Mater. 2012, 24, 6335–6341.

(42) Chen, W.; Nikiforov, M. P.; Darling, S. B. Morphology characterization in organic and hybrid solar cells. Energy Environ. Sci. 2012, 5, 8045–8074.

(43) Kovalenko, A.; Guerrero, A.; Garcia-Belmonte, G. Role of vertical segregation in semitransparent organic photovoltaics. ACS Appl. Mater. Interfaces 2015, 7, 1234–1239.

(44) Vohra, V.; Arrighetti, G.; Barba, L.; Higashimine, K.; Porzio, W.; Murata, H. Enhanced Vertical Concentration Gradient in Rubbed P3HT:PCBM Graded Bilayer Solar Cells. J. Phys. Chem. Lett. 2012, 3, 1820–1823.

(45) Melzer, C.; Koop, E. J.; Mihaleitchi, V. D.; Blom, P. W. M. Hole transport in poly(phenylene vinylene)/methanofullerene bulk-heterojunction solar cells. Adv. Funct. Mater. 2004, 14, 865–870.