| Title | High-performance ternary blend all-polymer solar cells with complementary absorption bands from visible to near-infrared wavelengths |
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| Author(s) | Benten, Hiroaki; Nishida, Takaya; Mori, Daisuke; Xu, Huajun; Ohkita, Hideo; Ito, Shinzaburo |
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Kyoto University
We developed high-performance ternary blend all-polymer solar cells with complementary absorption bands from visible to near-infrared wavelengths. A power conversion efficiency of 6.7% was obtained with an external quantum efficiency over 60% both in the visible and near-infrared regions. Our results demonstrate that the ternary blend all-polymer systems open a new avenue for accelerating improvement in the efficiency of non-fullerene thin-film polymer solar cells.

Organic photovoltaics have gained increasing attention as an inexpensive source of renewable energy owing to their unique advantages including high throughput and large-area production with low-cost printing processes. The power conversion efficiencies (PCEs) of organic thin-film solar cells have made significant progress over the past decade, and approached 10% in single-junction cells. The most widely studied solar cells consist of a bulk-heterojunction (BHJ) structure in which a conjugated polymer is mixed with a low-molecular-weight fullerene derivative. In the systems, the conjugated polymer acts as an electron donor and the fullerene derivative acts as an electron acceptor. On the other hand, polymer/polymer blend BHJ solar cells that utilize conjugated polymers as both an electron donor and an electron acceptor have recently attracted much attention because they have numerous potential advantages over conventional fullerene-based solar cells, though the polymer/polymer blend systems still lag behind their polymer/fullerene counterparts in power conversion efficiencies (PCEs). Herein, we report high-performance ternary blend all-polymer solar cells in which a wide-bandgap visible polymer is introduced as a third polymer into a low-bandgap near-infrared donor/acceptor binary polymer blend. Owing to the complementary absorption bands of the ternary blend, the PCE is improved up to 6.7% with an external quantum efficiency over 60% both in the visible and near-infrared regions. Our results demonstrate that the ternary blend all-polymer solar cells open a new avenue for accelerating improvement in the efficiency of non-fullerene thin-film OPVs.
complementary absorption bands but also sufficient free carrier generation and effective charge transport properties of both constituent binary blends. Unlike the case with polymer/PCBM systems, there are few such ideal binary polymer/polymer blends that work well individually at different wavelength ranges, while they share the common polymer acceptor.

In this study, we have designed ternary blend all-polymer solar cells in which a wide-bandgap polymer, poly[N9′-heptadecanoyl-2,7-carbazole-alt-3,5-(4′,7′-di-2-thienyl-2′,1′,3′-benzo thiadiiazole)] (PCDTBT), is introduced as a second donor into the highly efficient low-bandgap PBDDTT-EF-T/N2200 blend. We found that PCDTBT can contribute to efficient photocurrent generation in the ternary blends even though photovoltaic performance is poor for PCDTBT/N2200 binary blends. As a result, we have developed high-performance ternary blend all-polymer solar cells with much better efficiency than the PBDDTT-EF-T/N2200 binary blend, with an enhanced EQE of 65–70% even at visible wavelengths, and with a PCE of 6.65%. These values are the highest reported for ternary blend all-polymer BHJ solar cells. Furthermore, these results provide the first example of enhanced performance in ternary blend all-polymer systems based on highly efficient polymer/polymer BHJ solar cells.

As shown in Fig. 1b, the ternary blends are capable of providing broad and strong absorption covering the range of wavelengths from the visible to NIR regions because PCDTBT has an absorption band in the visible region that is complementary to the other two polymers, PBDDTT-EF-T and N2200.

The ternary blend polymer solar cell, which is fabricated by blending a second polymer donor or a dye molecule into a binary blend of a polymer donor and a [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) acceptor, is emerging as a fascinating alternative for broadening the absorption bandwidth of the photoactive layer.11,12 Owing to the advantage of overcoming the absorption limitation, the ternary blends based on wide- and low-bandgap donor polymers and PCBM have been investigated to achieve a PCE higher than that of the original binary polymer/PCBM solar cells.13,14 However, this concept has not been widely applied to enhance the efficiency of polymer/polymer BHJs,15 because such ternary blend systems require not only
device with 10 wt% PCDTBT; the device parameters were a $J_{SC}$ of 14.4 mA cm$^{-2}$, an $V_{OC}$ of 0.790 V, and a FF of 0.583. For comparison, $J-V$ curves and EQE spectra for the PBDTTT-EF-T/N2200 binary (solid circles) and PCDTBT/N2200 binary (open squares) blends are also shown in the figure, and the photovoltaic parameters of these devices are summarized in Table 1. Herein, we note that the device performance of the PBDTTT-EF-T/PCDTBT binary blend was much poorer than that of the PCDTBT/N2200 binary blend, with a $J_{SC}$ of 0.118 mA cm$^{-2}$ and a PCE of 0.042% (ESI† Fig. S2), indicating that PBDTTT-EF-T/PCDTBT heterojunctions are unsuitable for charge generation. The origin of the enhanced $J_{SC}$ for the ternary blends can be deduced from the EQE spectra. For the PBDTTT-EF-T/N2200 binary device, the EQEs were limited to 50% in the visible range from 500 to 600 nm. For the ternary device, the EQEs were improved noticeably mainly in the visible wavelengths, approaching values as high as 65–70%. Improvement in the EQEs at the PCDTBT absorption wavelength demonstrates that the increase in $J_{SC}$ for the ternary device is caused by the additional light absorption of PCDTBT. In addition, we note that the existence of EQEs higher than 60% at the NIR wavelengths reveals that the photovoltaic conversion through direct light absorption by both PBDTTT-EF-T and N2200 host polymers remained as excellent as that of the individually optimized PBDTTT-EF-T/N2200 binary blend, which is an essential prerequisite for improving overall device efficiency. As shown in Fig. 5, the photoluminescence (PL) spectrum of PCDTBT overlaps well with the absorption spectra of both PBDTTT-EF-T and N2200, giving a Förster radius ($R_0$) of 3.5 nm for PCDTBT to PBDTTT-EF-T and 3.3 nm for PCDTBT to N2200 (ESI† Fig. S3). Therefore, in addition to the enhanced light absorption by PCDTBT, in the ternary blends, resonant Förster energy transfer should occur from the wide-bandgap visible polymer PCDTBT to the low-bandgap NIR host polymers, PBDTTT-EF-T and N2200, after the light-absorption by PCDTBT. The energy transfer enables long-range transport of PCDTBT excitons directly to both PBDTTT-EF-T and N2200. To unravel the mechanism whereby our ternary blend system functioned

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**Fig. 2** (a) Estimated total film thickness and composition ratio of the constituent polymers in the PBDTTT-EF-T/N2200/PCDTBT ternary blend films plotted against the loading amount of PCDTBT. D, A, and T represent PBDTTT-EF-T, N2200, and PCDTBT, respectively. (b) Absorption spectra of PBDTTT-EF-T/N2200 binary blend (solid circles) and PBDTTT-EF-T/N2200/PCDTBT ternary blend films that contained 5 wt% (inverted triangles), 10 wt% (squares), 20 wt% (triangles), and 30 wt% (open circles) of PCDTBT.

**Fig. 3** Photovoltaic parameters ($J_{SC}$, $V_{OC}$, FF, and PCE) of PBDTTT-EF-T/N2200 binary and PBDTTT-EF-T/N2200/PCDTBT ternary BHJ solar cells measured under AM1.5G illumination from a calibrated solar simulator with an intensity of 100 mW cm$^{-2}$. The broken lines represent the photovoltaic parameters of these devices are summarized in Table 1. Herein, we note that the device performance of the PBDTTT-EF-T/PCDTBT binary blend was much poorer than that of the PCDTBT/N2200 binary blend, with a $J_{SC}$ of 0.118 mA cm$^{-2}$ and a PCE of 0.042% (ESI† Fig. S2), indicating that PBDTTT-EF-T/PCDTBT heterojunctions are unsuitable for charge generation. The origin of the enhanced $J_{SC}$ for the ternary blends can be deduced from the EQE spectra. For the PBDTTT-EF-T/N2200 binary device, the EQEs were limited to 50% in the visible range from 500 to 600 nm. For the ternary device, the EQEs were improved noticeably mainly in the visible wavelengths, approaching values as high as 65–70%. Improvement in the EQEs at the PCDTBT absorption wavelength demonstrates that the increase in $J_{SC}$ for the ternary device is caused by the additional light absorption of PCDTBT. In addition, we note that the existence of EQEs higher than 60% at the NIR wavelengths reveals that the photovoltaic conversion through direct light absorption by both PBDTTT-EF-T and N2200 host polymers remained as excellent as that of the individually optimized PBDTTT-EF-T/N2200 binary blend, which is an essential prerequisite for improving overall device efficiency.

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**Fig. 4** (a) $J-V$ characteristics of PBDTTT-EF-T/N2200/PCDTBT ternary (open circles), PBDTTT-EF-T/N2200 binary (solid circles), and PCDTBT/N2200 binary (open squares) BHJ solar cells measured under AM1.5G illumination from a calibrated solar simulator with an intensity of 100 mW cm$^{-2}$. The broken lines represent the $J-V$ characteristics under dark conditions. The loading amount of PCDTBT in the ternary blend was 10 wt%. (b) EQE spectra of the devices: PBDTTT-EF-T/N2200/PCDTBT (open circles), PBDTTT-EF-T/N2200 (solid circles), and PCDTBT/N2200 (open squares).
so beautifully, we focus on the charge generation from the excited states of PBDTTT-EF-T and N2200 even when light is absorbed by PCDTBT because PCDTBT excitons should be collected to PBDTTT-EF-T and N2200 by long-range exciton transport as mentioned above. Indeed, the PL of PCDTBT was completely quenched in the ternary blends regardless of the loading amount of PCDTBT ranging from 0 to 30 wt%, suggesting that all of the PCDTBT excitons are utilized for the charge generation [ESI,† Fig. S4]. Firstly, the PBDTTT-EF-T excited state is not quenched at the interface with PCDTBT, owing to the negligible energy offset between the lowest unoccupied molecular orbital (LUMO) levels of PBDTTT-EF-T and PCDTBT (Fig. 1c and ESI,† Fig. S5a, b). The non-quenching of PBDTTT-EF-T excitons at the heterojunction with PCDTBT is consistent with the result of negligible $J_{sc}$ values for the PBDTTT-EF-T/PCDTBT binary device (ESI,† Fig. S2). Therefore, PBDTTT-EF-T excitons, which are generated both directly by the NIR-light absorption and indirectly through the energy transfer from PCDTBT, can be converted to free charge carriers at the PBDTTT-EF-T/N2200 interface as efficiently as those in the case of the PBDTTT-EF-T/N2200 binary blends. The holes and electrons are transported through the PBDTTT-EF-T and N2200 networks, respectively, to the electrodes. Secondly, the N2200 excited state is quenched to form charges at the interfaces with PCDTBT, owing to an energy offset of 0.5 eV between the highest occupied molecular orbital (HOMO) levels of N2200 and PCDTBT (Fig. 1c). Here, the hole transfer from the N2200 excited state to PCDTBT will proceed in competition with charge generation at the other PBDTTT-EF-T/N2200 interface.

The energy diagram suggests that the resulting holes on PCDTBT at the PCDTBT/N2200 interfaces can migrate towards PBDTTT-EF-T, owing to the preferred cascade alignment of the HOMO energy levels of PCDTBT and PBDTTT-EF-T (Fig. 1c). Therefore, they can be transported as holes of PBDTTT-EF-T through the high-hole-mobility PBDTTT-EF-T networks to the electrode rather than being energetically trapped in relatively low-hole-mobility PCDTBT domains. Consequently, the quenching of N2200 excitons at the PCDTBT/N2200 interface does not necessarily result in hole trapping but contributes to photocurrent generation. The efficient collection of PCDTBT excitons by long-range resonant energy transfer and the rational alignment of the HOMO–LUMO energy levels of PCDTBT that minimizes quenching losses of both PBDTTT-EF-T and N2200 excitons are keys for improving the EQEs in the visible region while retaining the excellent EQE values at the NIR wavelengths.

To confirm this scenario, we further examine the dependence of the photocurrent on the applied reverse (negative) voltage in the ternary blends with the best PCE. Fig. 6 shows the net photocurrent density ($J_{ph}$) of the PBDTTT-EF-T/N2200/PCDTBT ternary (open circles), PBDTTT-EF-T/N2200 binary (solid circles), and PCDTBT/N2200 binary (open squares) BHJ solar cells under AM 1.5G illumination at 100 mW cm$^{-2}$. Here, $J_{ph}$ is given by $J_{ph} = J_{L} - J_{D}$, where $J_{L}$ and $J_{D}$ are the current densities under illumination and in the dark, respectively. It is worth noting that the PCDTBT/N2200 binary blend showed noticeable dependence of $J_{ph}$ on the applied reverse voltage, suggesting poor efficiency of either charge dissociation (dissociation of bound electron–hole pairs) into free carriers or charge carrier transport, or both. On the other hand, the PBDTTT-EF-T/N2200/PCDTBT ternary blend showed a weak dependence of $J_{ph}$ on the applied reverse voltage, and the $J_{ph}$ was saturated at reverse voltage higher than $-8$ V just as in the case of the PBDTTT-EF-T/N2200 binary blend, suggesting that all of the photogenerated free charge carriers in the devices were collected at the reverse voltage higher than $-8$ V. The increase in the reverse saturation photocurrent density $J_{ph,sat}$ ($\Delta J_{SAT} \Delta$) was 1.81 mA cm$^{-2}$, which agrees well with the increase in $J_{SC}$ ($\Delta J_{SC}$) of 1.72 mA cm$^{-2}$ this agreement indicates that the additional free charge carriers resulting from the PCDTBT light absorption are free from bimolecular recombination loss and hence are efficiently collected under short circuit conditions. The overall charge collection efficiencies under short-circuit conditions, which are defined as the ratio of $J_{SC}$ to $J_{ph,sat}$, were estimated to be as high as 84% in the ternary blend and 83% in the binary blend.

Table 1 Photovoltaic parameters of the PBDTTT-EF-T/N2200/PCDTBT ternary, PBDTTT-EF-T/N2200 binary, and PCDTBT/N2200 binary BHJ solar cells. The PCDTBT loading amount in the ternary blend was 10 wt%. The $J_{SC}$ calculated from the EQE spectrum, and the error between calculated (calc.) and measured $J_{SC}$ is also shown.

| Device | $J_{SC}$ (mA cm$^{-2}$) | $V_{OC}$ (V) | FF | PCE (%) | $J_{SC}$ (calc.) (mA cm$^{-2}$) | Error (%) |
|--------|-------------------------|-------------|-----|---------|-------------------------------|----------|
| Ternary PBDTTT-EF-T/N2200/PCDTBT | 14.4 (14.3 ± 0.18) | 0.790 (0.790 ± 0.00) | 0.583 (0.570 ± 0.01) | 6.65 (6.45 ± 0.11) | 14.7 | 2.1 |
| Binary PBDTTT-EF-T/N2200 | 12.4 (12.7 ± 0.24) | 0.806 (0.801 ± 0.00) | 0.568 (0.542 ± 0.01) | 5.70 (5.49 ± 0.10) | 12.8 | 3.2 |
| Binary PCDTBT/N2200 | 2.00 (1.76 ± 0.11) | 0.970 (0.959 ± 0.06) | 0.397 (0.370 ± 0.01) | 0.77 (0.634 ± 0.06) | 1.94 | 3.0 |

$\Delta$ The values are the photovoltaic parameters of solar cells with the highest PCEs. Averaged values over at least 14 devices are shown in parentheses.
These results demonstrate that the charge collection in the PBDTTT-EF-T/N2200/PCDTBT ternary BHJ solar cells can be as efficient as in the PBDTTT-EF-T/N2200 binary BHJ solar cells even though poor charge dissociation and/or transport is expected from the PCDTBT/N2200 binary BHJ solar cells. In other words, the PBDTTT-EF-T/N2200/PCDTBT ternary BHJ solar cell functioned well by taking full advantage of the excellent free carrier generation and transport capabilities of the PBDTTT-EF-T/N2200 binary BHJ.

Finally, we examine the dependence of \( J_{ph,sat} \) and charge carrier mobilities on the amount of PCDTBT loading. As shown in Fig. 7a, we found that the overall charge collection efficiency under short-circuit conditions remained close to 80% even for the ternary blend containing 20 wt% PCDTBT. Fig. 7b shows \( \mu_h \) and \( \mu_e \) determined using the space-charge-limited current (SCLC) method with the Mott-Gurney equation. The \( \mu_h \) increased from 4.3 \( \times 10^{-3} \) cm\(^2\) V\(^{-1}\) s\(^{-1}\) in the PBDTTT-EF-T/N2200 binary blend to 1.3 \( \times 10^{-3} \) cm\(^2\) V\(^{-1}\) s\(^{-1}\) in the ternary blend containing 30 wt% PCDTBT, which is much larger than that of PCDTBT neat film (on the order of \( 10^{-5} \) cm\(^2\) V\(^{-1}\) s\(^{-1}\)). These results support our proposed mechanism that the bottleneck of charge-transport of the PCDTBT/N2200 binary device is overcome by energetically-feasible hole transfer from PCDTBT to PBDTTT-EF-T. On the other hand, the \( \mu_e \) was found to decrease by an order of magnitude from 7.0 \( \times 10^{-4} \) cm\(^2\) V\(^{-1}\) s\(^{-1}\) in the binary blend to 6.9 \( \times 10^{-5} \) cm\(^2\) V\(^{-1}\) s\(^{-1}\) in the ternary blend containing 30 wt% PCDTBT, resulting in an imbalance between hole and electron mobilities. As shown in Fig. 3, the decrease in \( J_{SC} \) and FF was observed for the ternary blend containing 30 wt% PCDTBT. Such a detrimental effect may be attributed to reduced charge collection efficiency caused by the increased film thickness of \( \sim 150 \) nm and the decreased electron mobility.

As shown in Fig. 4 and 6, the second polymer donor PCDTBT forms BHJs with N2200 that exhibit limited photovoltaic performance and different \( V_{OC} \) values from the PBDTTT-EF-T/N2200 binary blend. However, our ternary blends composed of 0–20 wt% PCDTBT improved the PCE while retaining similar values of \( J_{SC}, J_{ph,sat}, V_{OC}, \) and FF to those of the PBDTTT-EF-T/N2200 host binary blend. The compositional dependence strongly suggests that PCDTBT contributed to the photogenerated current as a visible sensitizer through efficient energy transfer for both PBDTTT-EF-T and N2200 rather than as a PCDTBT/N2200 device working in parallel with the PBDTTT-EF-T/N2200. In this case, PCDTBT absorbs visible light but relies on both PBDTTT-EF-T and N2200 host polymers to generate and transport free charge carriers. As a result, improvement in the PCE can be achieved by taking full advantage of the excellent photovoltaic conversion characteristics of the PBDTTT-EF-T/N2200 binary blend.

Conclusions

We have demonstrated that the PCE of low-bandgap PBDTTT-EF-T/N2200 binary BHJ solar cells can be improved by introducing wide-bandgap PCDTBT to complement the weak absorption at visible wavelengths. For the ternary blend all-polymer BHJ solar cell containing 10 wt% PCDTBT, the EQEs at visible wavelengths were successfully increased up to 65–70%, and a PCE as high as 6.65% was obtained. These values are the highest reported for ternary blend all-polymer BHJ solar cells. In the ternary blends, PCDTBT excitons can be transported directly to both PBDTTT-EF-T and N2200 through long-range resonant Förster energy transfer, contributing to the photocurrent generation as a visible sensitizer. Consequently, light absorption by PCDTBT can lead to an increase in \( J_{SC} \), by taking advantage of the excellent free carrier generation and transport characteristics of the PBDTTT-EF-T/N2200 binary blends. Our results demonstrate that the use of ternary blends composed of a wide-bandgap polymer along with an efficient low-bandgap donor/acceptor polymer blend is an effective strategy for achieving more efficient all-polymer BHJ solar cells. This approach should be applicable to the recently reported low-bandgap donor/acceptor polymer BHJ solar cells with the highest level of PCEs. The ternary blend all-polymer BHJs open a new avenue for accelerating improvement in the efficiency of non-fullerene thin-film polymer solar cells.

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