Photon Energy Loss in Ternary Polymer Solar Cells Based on Nonfullerene Acceptor as a Third Component

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Abstract

Understanding photon energy loss caused by the charge recombination in ternary blend polymer solar cells based on nonfullerene acceptors (NFAs) is crucial for achieving further improvements in their device performance. However, such a ternary system that the two types of donor/acceptor (D/A) interface coexist makes it more difficult to analyze the photon energy loss. Here, we have focused on the origin of the voltage loss behind a high open-circuit voltage (*V*OC) in ternary blend devices based on one donor polymer (PTzBT) and two acceptors, including a fullerene derivative (PCBM) and an NFA (IEICO-4F), which exhibit *V*OC similar to that of fullerene-based PTzBT/PCBM binary devices. From the temperature dependent *V*OC, we found that the effective interfacial bandgap is the same between them: the PTzBT/PCBM/IEICO-4F ternary blend device is close to the PTzBT/PCBM fullerene-based binary device rather than the PTzBT/IEICO-4F nonfullerene-based binary device. This means that the recombination center of ternary blend device is still the interface of PTzBT/PCBM regardless of incorporation of a small amount of NFA. On the basis of detailed balance theory, we found that the radiative and nonradiative recombination voltage loss for PTzBT/PCBM/IEICO-4F ternary devices significantly reduced compared to the that of fullerene-based PTzBT/PCBM binary counterparts. This is ascribed to the disappearance of charge transfer absorption due to overlap with the absorption of NFA and the reduction of energetic disorder due to the incorporation of NFA.

1. Introduction

Recently, polymer solar cells have received the spotlight once again in photovoltaic community since diverse nonfullerene acceptor (NFA) molecules with near infrared absorption bands have been employed as an acceptor. This is because the power conversion efficiency (PCE) of these single junction binary devices has shot up from 12% to more than 19% with keeping their exceptional advantages, including flexibility and a low-cost fabrication by solution processes.1–10 However, this PCE still lags far behind that for lead-based perovskite solar cells or inorganic solar cells based on III-V compound semiconductors, i.e. GaAs, mainly due to lower open-circuit voltage (*V*OC) and/or short-circuit current density (*J*SC), respectively.11 As such, strategies not only for enhancing the light-harvesting efficiency for high *J*SC but also for suppressing the photon energy loss (*E*loss = *E*gPV – *qV*OC) from optical bandgap energy of photovoltaic (*E*gPV) for high *V*OC at the same time are an essential prerequisite for highly efficient polymer solar cells toward commercialization. To satisfy these objectives, ternary blends incorporating NFA as a third component can be an attractive and simple approach. It is clear that an improvement in *J*SC for ternary blends can be realized by using materials with the complementary absorption bands over a wide wavelength region due to the increased light-harvesting efficiency.12–14 On the other hand, the mechanism behind *V*OC improvements would be complicated because *V*OC is considerably dependent upon the donor/acceptor (D/A) interfaces for the ternary devices. In particular, it is unclear which interface serves as the recombination center in the ternary system including a small amount of NFA. Accordingly, analyzing *E*loss for these ternary devices is still controversial, even though it appears to be much lower for NFA-based binary devices compared to fullerene-based binary counterparts as a result of a reduced recombination voltage loss.15–18 Therefore, many questions about how to obtain high *V*OC in ternary systems based on NFA still remain unanswered as the origin of their *E*loss is not fully understood.

In this study, we have discussed the origin of *E*loss behind high *V*OC in ternary polymer solar cells based on blends of a donor conjugated polymer, a fullerene derivative acceptor and a small fraction of NFA in comparison with both fullerene- and NFA-based binary counterparts. As shown in **Figure 1**, we employed poly(2,5-bis(3-dodecylthiophen-2-yl)-thiazolo[5,4-*d*]thiazole) (PTzBT) as a wideband gap donor polymer with a high crystallinity,19–21 [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) as a fullerene acceptor, and (2,2’-((2Z,2’*Z*)-(((4,4,9,9-tetrakis(4-hexylphenyl)-4,9-dihydro-sindaceno[1,2-*b*:5,6-*b*’]dithiophene-2,7-diyl)bis(4-((2-ethylhexyl)oxy)thiophene-5,2-diyl))bis(methanylylidene))bis(5,6-difluoro-3-*oxo*-2,3-dihydro-1*H*-indene-2,1-diylidene))dimalononitrile) (IEICO-4F) as an NFA. Interestingly, ternary devices incorporating only 6 wt% of NFA exhibit *V*OC as high as fullerene-based binary devices, which suggest dominant interface would be still PTzBT/PCBM interface. On the other hands, the *E*loss for ternary systems was evaluated to be 0.54 eV as low as that of NFA binary devices, which is more suppressed compared to fullerene-based binary blend devices (1.05 eV). This is attributed to the variation in *E*gPV along with the introduction of low bandgap IEICO-4F. From the temperature dependent *V*OC, we found that the effective bandgap at the donor/acceptor interface (*E*geff) that is the recombination center of ternary device is the polymer/fullerene interface, indicating unchanged recombination center despite of the introduction of NFA. In addition, we further delve into the differences in loss components ascribed to charge recombination, i.e. radiative and nonradiative voltage losses, quantitatively by analyzing recombination voltage loss on the basis of detailed balance theory.23 As a result, both radiative and nonradiative recombination voltage losses for ternary device are significantly reduced compared to the fullerene-based binary counterparts. This is attributed to the disappearance of charge transfer (CT) state due to incorporation of IEICO-4F with a reduced energetic disorder. We believe that this research will serve as watershed moment for highly efficient ternary polymer solar cells.

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**Figure 1.** Chemical structures of (a) PTzBT, (b) PCBM, and (c) IEICO-4F.

2. Results and Discussion

2.1. Photovoltaic performance and photon energy loss

In this study, we fabricated three kinds of polymer solar cells with an inverted device structure of ITO/ZnO/photoactive layer/MoO*x*/Au. The blend composition employed is as follows: PTzBT/PCBM (1:2 w/w), PTzBT/IEICO-4F (1:1.5 w/w), and PTzBT/PCBM/IEICO-4F (1:2:0.2 w/w). The *J–V* characteristics of the devices, measured under stimulated AM 1.5G solar illustration at 100 mW cm–2, are illustrated in **Figure 2(a)**, and the corresponding photovoltaic parameters are summarized in **Table 1**.

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**Figure 2.** (a) *J–V* characteristics under AM 1.5G simulated solar illumination with 100 mW cm–2 and (b) external quantum efficiency spectra of PTzBT-based polymer solar cells: PTzBT/PCBM (black), PTzBT/IEICO-4F (blue), and PTzBT/PCBM/IEICO-4F (red).

**Table 1.** Photovoltaic parameters of PTzBT-based polymer solar cells.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Blend | *J*SC / mA cm–2 | *V*OC / V | FF | PCE / % |
| PTzBT/PCBM | 11.3 | 0.88 | 0.64 | 6.4 |
| PTzBT/IEICO-4F | 3.5 | 0.80 | 0.52 | 1.4 |
| PTzBT/PCBM/IEICO-4F | 8.0 | 0.88 | 0.56 | 3.9 |

Although the PTzBT/PCBM/IEICO-4F ternary devices showed higher PCE than PTzBT/IEICO-4F binary devices, it is still lower than that of PTzBT/PCBM binary devices despite introducing IEICO-4F as a third component able to absorb the near-infrared region of solar spectrum. This is mainly ascribed to lower *J*SC and FF. As shown in **Figure 2(b)**, the difference in *J*SC between PTzBT/PCBM binary and PTzBT/PCBM/IEICO-4F ternary devices results from the significantly decreased EQEPV in the region of PTzBT absorption band.From photoluminescence (PL) quenching efficiency under selective excitation of PTzBT, we found efficient energy and/or charge transfer from donor to acceptor for all the blends employed in this study (**Figure S1**). In addition, as illustrated in **Figure S2**, PTzBT/PCBM binary devices exhibit the saturated photocurrent density, while no saturated photocurrent density observed for the PTzBT/IEICO-4F binary and PTzBT/PCBM/IEICO-4F ternary devices even under −5 V bias where all the photogenerated carriers would be collected.22 These results suggest inefficient charge dissociation and/or collection efficiency for PTzBT/IEICO-4F binary and PTzBT/PCBM/IEICO-4F ternary devices.

On the other hand, no difference in *V*OC was observed between the PTzBT/PCBM binary and PTzBT/PCBM/IEICO-4F ternary devices. Specifically, the PTzBT/PCBM binary and PTzBT/PCBM/IEICO-4F ternary devices showed a *V*OC of 0.88 V, whereas it is as low as 0.8 V for the PTzBT/IEICO-4F binary devices. In particular, slightly lower energy level of the lowest unoccupied molecular orbital (LUMO) in IEICO-4F compared to that of PCBM is observed as shown in **Figure S3**. It should be note that *V*OC varies with IEICO-4F compositions for these devices (**Figure S4 and Table S1**), indicating that the variation in *V*OC is conjectured to be related to different recombination centers in accordance with blend ratios. As such, we have focused on the origin of *E*loss underlying high *V*OC in this ternary device rather than the overall photovoltaic parameters in this research. Firstly, we evaluated the *E*gPV from the peak of the differential EQEPV spectra as illustrated in **Figure S5**.23 The value of *E*gPV of PTzBT/PCBM/IEICO-4F ternary devices was estimated to be 1.42 eV, which is considerably smaller than that (1.93 eV) of PTzBT/PCBM binary devices and close to that (1.36 eV) of PTzBT/IEICO-4F binary devices. On the basis of this value evaluated, we next calculated *E*loss for each blend. As a result, *E*loss was extremely suppressed down to 0.54 eV for PTzBT/PCBM/IEICO-4F ternary devices, which is as small as that for PTzBT/IEICO-4F binary devices (0.56 eV) compared to PTzBT/PCBM binary devices (1.05 eV). These results suggest that incorporating small amount of IEICO-4F contributes to reducing *E*loss without suppressing *V*OC. We will further discuss whether such a huge difference in *E*loss could be attributed or not to variation in interfacial CT state and/or reduced voltage loss caused by charge recombination.

2.2. Interfacial charge transfer state and recombination center

To examine the interfacial CT state in each blend, we next measured the temperature dependence of *V*OC to address the origin of recombination center for each device. As reported previously,24–28 *qV*OC is expressed as

 (1)

where *q* is the elementary charge, *E*geff is the interfacial effective bandgap, *N*0 is the effective density of electronic states, and *n* and *p* are the density of electrons and holes, respectively. The first term in the equation (1) is a measure of an energetic level of interfacial CT state in working devices, which is independent of temperature while the second term is dependent upon temperature. Therefore, we can distinguish the recombination center for each device. To be specific, if the *E*geff of the PTzBT/PCBM/IEICO-4F ternary device is the same as that of PTzBT/PCBM binary device, the recombination center would be the PTzBT/PCBM interface in the ternary blends. On the other hand, if it is in good agreement with that of PTzBT/IEICO-4F binary device, its center would be the PTzBT/IEICO-4F interface in the ternary blends. Here, the first term *E*geff can be obtained as an intercept of the linear extrapolation of *qV*OC at 0 K. **Figure 3** shows the temperature dependence of *qV*OC for each device and the corresponding *E*geff and their energy loss *q*Δ*V*rec were summarized in **Table 2**. As a result, it was evaluated to be 1.30 eV for the PTzBT/PCBM binary and 1.18 eV for the PTzBT/IEICO-4F binary devices. Interestingly, the *E*geff of the PTzBT/PCBM/IEICO-4F ternary device converged to the exactly same value of the PTzBT/PCBM binary device. These results suggest the recombination center in ternary device is still the interface of PTzBT/PCBM in spite of the incorporation of a small amount of IEICO-4F. We next disclose voltage loss components incurred by radiative and nonradiative recombinations on the basis of detailed balance theory.23

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**Figure 3.** Temperature dependence of *qV*OC for PTzBT-based polymer solar cells: PTzBT/PCBM (black), PTzBT/IEICO-4F (blue), and PTzBT/PCBM/IEICO-4F (red). Each solid line represents the extrapolation of temperature dependence of *qV*OC.

**Table 2.** Interfacial effective bandgap *E*geff and their energy loss *q*Δ*V*rec for PTzBT-based polymer solar cells.

|  |  |  |  |
| --- | --- | --- | --- |
| Blend | *E*geff / eV | *qV*OC / eV | *q*Δ*V*rec |
| PTzBT/PCBM | 1.30 | 0.88 | 0.42 |
| PTzBT/IEICO-4F | 1.18 | 0.80 | 0.38 |
| PTzBT/PCBM/IEICO-4F | 1.30 | 0.88 | 0.42 |

2.3. Radiative and nonradiative voltage losses

To discuss voltage loss components for the polymer solar cells, we analyzed EQEPV and EL spectra on the basis of the detailed balance theory. According to Kirchartz and Rau,23 the *V*OC is given by

 (2)

where Δ*V*SQ = *E*gPV/*q* –  and the superscripts “SQ” represents the Shockley–Queisser limit. Here, *J*SCSQ, *J*0SQ, *J*SC, and *J*0rad are given by the following equations, respectively.

 (3)

 (4)

 (5)

 (6)

where ΦAM1.5G and ΦBB denote the AM1.5G solar spectrum and blackbody spectrum at *T* = 300 K of the solar cell, respectively. In the SQ framework, the voltage loss caused by radiative charge recombination is the thermodynamically inevitable loss for photovoltaic devices.29–32 The other terms Δ*V*SC, Δ*V*r, and Δ*V*nr are additional voltage losses as follows: The Δ*V*SC results from the smaller *J*SC than the theoretical vale *J*SCSQ that all the solar light above *E*g converts to photocurrent with an efficiency of 100%. This loss is typically negligibly small. The Δ*V*r arises from radiative recombination due to the absorption below *E*gPV such as CT absorption band and energetic exponential tail. The Δ*V*nr is ascribed to nonradiative recombination loss, which corresponds to the difference between the actual *V*OC of solar cells and  in the radiative limit. The results of the voltage loss analysis are summarized in **Table 3**. As mentioned above, Δ*V*SC is negligibly small and no significant difference between all the devices. In contrast, there is a stark difference in Δ*V*r between PTzBT/PCBM binary device and the other devices. The larger Δ*V*r (0.37 V) for PTzBT/PCBM binary devices is due to the pronounced CT absorption below the *E*gPV as shown in **Figure 4**, while the PTzBT/IEICO-4F binary and PTzBT/PCBM/IEICO-4F ternary devices exhibit a very small Δ*V*r of 0.01 and 0.002 V, respectively. This is attributable to the steep absorption edge due to the disappearance of the CT absorption below the *E*gPV. Lastly, the Δ*V*nr for PTzBT/PCBM binary devices was as high as 0.38 V, while it was as small as 0.21 V for PTzBT/IEICO-4F binary devices and 0.25 V for PTzBT/PCBM/IEICO-4F ternary devices. Such a reduced Δ*V*nr in PTzBT/PCBM/IEICO-4F ternary devices is ascribed to the suppressed energetic disorder by incorporating a small amount of IEICO-4F, as will be discussed later. As a results, suppressed *E*loss in ternary blend devices is achieved from both reduced radiative and nonradiative recombination losses.

**Table 3.** *E*gPV ,*V*OC, and the corresponding voltage loss components for PTzBT-based polymer solar cells.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Blend | *E*gPV/ eV | *V*OC / V | Δ*V*SQ */* V | Δ*V*SC */* V | Δ*V*r  / V | Δ*V*nr / V |
| PTzBT/PCBM | 1.93 | 0.88 | 0.28 | 0.02 | 0.37 | 0.38 |
| PTzBT/IEICO-4F | 1.36 | 0.80 | 0.25 | 0.06 | 0.002 | 0.25 |
| PTzBT/PCBM/IEICO-4F | 1.42 | 0.88 | 0.26 | 0.03 | 0.01 | 0.24 |

2.4. Energetic disorder

To further discuss the origin of reduced Δ*V*nr in ternary blend systems, we examined an energetic disorder below the *E*gPV for each blend. As reported previously,33–36 the nonradiative recombination is directly correlated to the energetic disorder of materials observed in the sub-bandgap region with an energetic exponential tail. For the disordered organic semiconductors, the EQEPV(*E*) in the sub-bandgap region is directly proportional to the absorption coefficient *α*(E), and hence, follows the Urbach rule: EQEPV(*E*) ∝ *α*(*E*) ∝ exp[(*E* – *E*gPV)/*E*U] where the *E*U is the Urbach energy.37 As the smaller *E*U, the steeper bandgap edge is observed. Therefore, *E*U is often regarded as a measure of energetic disorder. On the basis of the exponential fit to the sub-bandgap of the EQEPV spectra (**Figure 4**), the *E*U was evaluated for each system. It should be noted that, as illustrated in **Figure 4**, the PTzBT/PCBM binary device exhibits the absorption of the polymer at high energies (>1.9 eV) followed by the distinct absorption shoulder of the PCBM at around 1.75 eV.38 Below the fullerene absorption shoulder, there is another component in the spectra likely representing the CT state absorption around 1.4 eV. Therefore, we evaluated the *E*U for both absorption edge of PTzBT and fullerene absorption shoulder (*E*UPCBM) for the PTzBT/PCBM binary device. For the other blends, there is no distinct absorption band in the sub-bandgap region. This result also supports reduced Δ*V*r for these blends attributed to the disappearance of the CT absorption as a result of the overlap with the IEICO-4F absorption. As a result, the it was evaluated to be 41 and 42 meV for the PTzBT/PCBM binary device, whereas it was as small as 25 and 23 meV for the PTzBT/IEICO-4F binary and PTzBT/PCBM/IEICO-4F ternary devices, respectively. These values are comparable to that of highly-ordered organic semiconductor blend systems exhibiting a high *V*OC with a suppressed recombination voltage loss.39–40 A markedly small *E*U in IEICO-4F-based devices is probably due to the significantly high crystallinity of IEICO-4F. According to previous reports,41–43 IEICO-4F molecules exhibit a planar geometry with a strong π–π stacking, which leads to highly ordered state. Consequently, the significantly reduced energetic disorder can effectively suppress the Δ*V*nr in the PTzBT/IEICO-4F binary and PTzBT/PCBM/IEICO-4F ternary devices.



**Figure 4.** Semilogarithmic plots of EQEPV spectra plotted against photon energy for PTzBT-based polymer solar cells: (a) PTzBT/PCBM, (b) PTzBT/IEICO-4F, and (c) PTzBT/PCBM/IEICO-4F blend devices. The blue and red solid lines are fitting ones by an exponential function, and the orange broken line is a fitting curve by a Gaussian function, respectively.

**Table 4.** Energetic disorder parameters for PTzBT-based polymer solar cells .

|  |  |  |
| --- | --- | --- |
| Blends | *E*U /meV | *E*UPCBM / meV |
| PTzBT/PCBM | 42 | 41 |
| PTzBT/IEICO-4F | 25 | – |
| PTzBT/PCBM/IEICO-4F | 23 | – |

3. Conclusions

In summary, we have examined the origin of *E*loss behind high *V*OC in ternary polymer solar cells consisting of one crystalline donor polymer PTzBT and two acceptors, inclusive of fullerene (PCBM) and nonfullenere (IEICO-4F) molecules. Interestingly, *E*loss for ternary device exhibits as small as 0.57 eV, which is significantly suppressed compared to the fullerene-based binary counterparts (1.05 eV). This implies that the incorporation of a small amount of IEICO-4F can effectively reduce *E*loss without suppressing *V*OC. With respect to the evaluation of *E*geff on the basis of temperature dependence of *V*OC, we found that high *V*OC in ternary device can be achieved because the recombination center for ternary device is still the interface of PTzBT/PCBM regardless of the incorporation of a small amount of IEICO-4F (6 wt%). On the basis of the detailed balance theory, we next analyzed voltage loss components caused by radiative and nonradiative recombination for each device. As a results, a decrease in *E*loss is attributable to suppressed Δ*V*nr as well as Δ*V*r upon an addition of small amount of IEICO-4F into the fullerene-based devices. To be specific, Δ*V*r for PTzBT/PCBM/IEICO-4F ternary devices was evaluated to be 0.01 V, which is definitely smaller than that for PTzBT/PCBM binary devices (0.37 V). This results from the disappearance of the CT absorption thanks to the overlap with the IEICO-4F absorption for ternary systems. Moreover, the values of Δ*V*nr were also considerably reduced for PTzBT/PCBM/IEICO-4F ternary systems compared to fullerene-based PTzBT/PCBM binary counterparts: it was lower by ~0.1 V for the ternary devices than that for fullerene-based binary devices. By evaluating the broadness of the absorption onset in the sub-bandgap region, we found that this is due to suppressed energetic disorder for ternary blend systems. This is conjectured to be caused by a planar geometry of IEICO-4F molecules, ultimately giving rise to strong π–πstacking and hence high crystallinity. As such, a high *V*OC incurred by low *E*loss for ternary blend systems could be achievable by adding a small amount of highly ordered NFA as a result of unchanged recombination center and reduced recombination voltage loss. We believe that this research offers a clear guidance for highly efficient ternary blend polymer solar cells.

4. Experimental section

*Materials*: PTzBT was synthesized according to the method reported previously.19 PCBM and IEICO-4F were purchased from Frontier carbon and 1-Materials, respectively. All of the materials were employed without further purification.

*Device Fabrication*: All the solar cells used in this study were fabricated with an inverted device structure of indium tin oxide (ITO)-coated glass substrate/zinc oxide (ZnO)/active layer/MoO*x*/Au. An electron-transporting layer (~20 nm) of ZnO was spin-coated on the cleaned ITO-coated glass substrate at 1200 rpm for 20 s from dispersed ZnO nanoparticle solution. Subsequently, these substrates were transferred into an inert glovebox under an inert atmosphere of nitrogen (H2O and O2 < 1 ppm). The binary and ternary active layers were prepared on top of ITO/ZnO substrates according to each fabrication condition, as summarized in **Table S2**. Finally, a metal electrode of MoO*x*/Au (7.5 nm/100 nm) was thermally evaporated through thermal deposition under pressure of 2.5 × 10–4 Pa.

*Measurements*: *J–V* characteristics were measured with a direct current (DC) voltage and current source/monitor (Keithley, 2611B) under the dark and illumination with AM 1.5G simulated solar light with 100 mW cm–2. The light intensity was calibrated using a standard silicon photodiode reference cell (Bunko-Keiki, BS-520). The EQEPV spectra were measured with a spectral response measurement system (Bunko-Keiki, ECT-250D). The power of incident monochromatic light kept under 0.05 mW cm–2, which was measured with a calibrated silicon reference cell (Bunko-Keiki, BS-520BK). Temperature dependence of the *J–V* characteristics was measured with a DC voltage and current source/monitor (Advantest, R6243) in a vacuum prober system (ALS Technology, VPS3-50) under the illumination from a 100 W Xe lamp (Asahi Spectra, LAX-RLQL80-0.5).

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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**Conflict of Interest**

The authors declare no conflict of interest.

**Data Availability Statement**

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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The table of contents entry should be 50–60 words long and should be written in the present tense. The text should be different from the abstract text.

Photon Energy Loss in Ternary Polymer Solar Cells Based on Nonfullerene Acceptor as a Third Component

Jihun Jeon, Shohei Hosoya, Masahiko Saito, Itaru Osaka, Hideo Ohkita\* and Hyung Do Kim\*

The origin of photon energy loss (*E*loss) behind high open-circuit voltage is investigated for ternary polymer solar cells based on IEICO-4F acceptor. By adding a small amount of IEICO-4F (6 wt%) into fullerene-based binary devices, *E*loss is significantly suppressed for ternary blend systems while maintaining the recombination center of polymer/fullerene interface. This is ascribable to a decrease in both radiative and nonradiative voltage losses via overshadowed charge transfer state and reduced energetic disorder in ternary blend solar cells.



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Supporting Information

Photon Energy Loss in Ternary Polymer Solar Cells Based on Nonfullerene Acceptor as a Third Component

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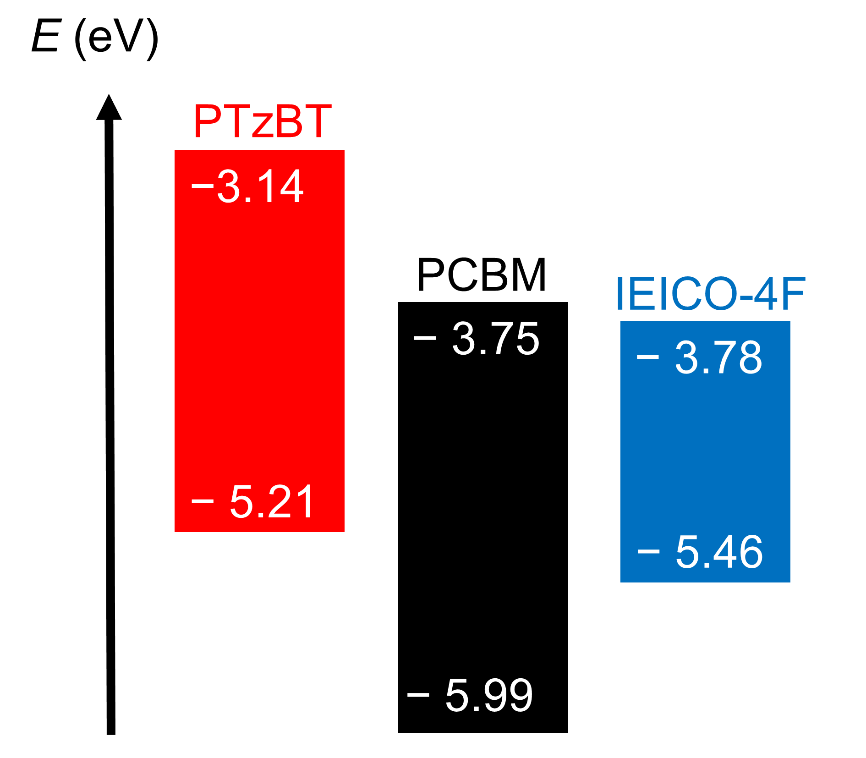
Hiroshima University 1-4-1 Kagamiyama, Higashi-Hiroshima, Hiroshima, 739-8527, Japan

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**Figure S1.** (a) Absorption spectra and (b) photoluminescence spectra for PTzBT-based neat and blend films: PTzBT (gray), PTzBT/PCBM (black), PTzBT/IEICO-4F (blue), and PTzBT/PCBM/IEICO-4F (red). The samples were excited at 550 nm for selective excitation of PTzBT polymer.



**Figure S2.** *J*ph plotted against to applied voltage for PTzBT-based polymer solar cells: PTzBT/PCBM (black), PTzBT/IEICO-4F (blue), and PTzBT/PCBM/IEICO-4F (red). *J*ph represents the photogenerated current density, *J*ph = *J*light – *J*dark.



**Figure S3.** Schematic illustration of energy diagrams for each material employed in this study.



**Figure S4.**  *J–V* characteristics of the PTzBT/PCBM/IEICO-4F polymer solar cells with different IEICO-4F ratio: 9 wt% (black), 15 wt% (blue), and 30 wt% (red).



**Figure S5.** EQEPV spectra (black solid line) and the differential EQEPV spectra (red solid line) of (a) PTzBT/PCBM, (b) PTzBT/IEICO-4F, and (c) PTzBT/PCBM/IEICO-4F solar cells as a function of energy. The *E*gPV was determined from a peak of the differential EQEPV spectra.



**Figure S6.** Temperature dependence of *J–V* curves for PTzBT-based polymer solar cells: (a) PTzBT/PCBM, (b) PTzBT/IEICO-4F, and (c) PTzBT/PCBM/IEICO-4F blend systems.



**Figure S7.** Normalized EL spectra for PTzBT-based polymer solar cells: PTzBT/PCBM (black), PTzBT/IEICO-4F (blue), and PTzBT/PCBM/IEICO-4F (red).

**Table S1.** Photovoltaic parameters of PTzBT-based devices with diverse IEICO-4F ratio.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| IEICO-4F content | *V*OC / V | *J*SC / mA cm–2 | FF | PCE / % |
| 9 wt% | 0.86 | 5.9 | 0.65 | 3.3 |
| 15 wt% | 0.85 | 5.1 | 0.63 | 2.7 |
| 30 wt% | 0.84 | 3.0 | 0.52 | 1.3 |

**Table S2.** Fabrication conditions for PTzBT-based polymer solar cells.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Blend | Solvent | Concentration  / wt% | Spin rate  / rpm | Spin temperature / ℃ |
| PTzBT/PCBM | CB | 1:2 | 500 | 100 |
| PTzBT/IEICO-4F | 1:1.5 | 1000 |
| PTzBT/PCBM/IEICO-4F | 1:2:0.2 | 500 |