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Enhance performance of organic solar cells based on an isoindigo-based copolymer by balancing absorption and miscibility of electron acceptor

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Superior absorption of PC₇₁BM in visible region to that of PC₆₁BM makes PC₇₁BM a predominant acceptor for most high efficient polymer solar cells (PSCs). However, we will demonstrate that power conversion efficiencies (PCEs) of PSCs based on poly[*N,N'*-bis(2-hexyldecyl)isoindigo-6,6'-diyl-*alt*-thiophene-2,5-diyl] (PTI-1) with PC₆₁BM as acceptor are 50% higher than their PC₇₁BM counterparts under illumination of AM1.5G. AFM images reveal different topographies of the blends between PTI-1:PC₆₁BM and PTI-1:PC₇₁BM, which suggests that acceptor's miscibility plays a more important role than absorption. The photocurrent of 9.1 mA/cm² is among the highest value in PSCs with a driving force for exciton dissociation less than 0.2 eV. © 2011 American Institute of Physics. [doi:10.1063/1.3645622]

Bulk-heterojunction (BHJ) polymer solar cells (PSCs) composed of two materials (donor and acceptor) are very attractive due to their advantages of low cost, solution process, and flexibility, though the commercialization is still limited by their low efficiency and short lifetime.¹⁻³ The performance of PSCs depends primarily on both material properties and device processing conditions.⁴ To improve the efficiency of PSCs, enormous efforts have been made through synthesizing new materials with preferable photo-physical properties, exploring new device structures and optimizing processing conditions.⁵⁻¹¹ Efficiently generating free charge carriers needs a large interface between donor and acceptor. On the other hand, extracting free charge carriers requires bi-continuous paths between two electrodes. The self-organized morphology of the active layers formed during solution process in PSCs is governed by the solubility and miscibility of two components. Realizing an optimal morphology for a high efficiency is a big challenge and an arduous task through exploring different processing parameters such as mixed solvents,¹² pre/post thermal treatment,^{13,14} and solvent annealing.^{13,15} Recently, various additives, especially diiodooctane (DIO), attracted considerable attention and become an efficient method to manipulate morphology of active layers for good performance PSCs.^{16,17} In most cases, high efficient PSCs are made by using PC₇₁BM as an acceptor instead of PC₆₁BM, for the absorption of PC₇₁BM in the visible region contributing a decent part to short-circuit current density (J_{sc}) and the PCE.^{2,5} However, the solubility of PC₇₁BM in some organic solvents is not as good as that of PC₆₁BM, so is its miscibility with some polymers.^{18,19} This may lead to an unfavorable morphology and deteriorate the performance of PSCs.

Recently, we reported PSCs based on an isoindigo-based polymer PTI-1 and PC₇₁BM, which demonstrated a PCE of 3.0%, a J_{sc} of 5.4 mA/cm² and an open-circuit volt-

age (V_{oc}) of 0.89 V.²⁰ The rather high V_{oc} is due to PTI-1's low lying HOMO level, although its band gap is as low as 1.6 eV. Another promising property of PTI-1 is its broad absorption spectrum from 300 to 800 nm containing three peaks with the highest one in 600-700 nm. We notice that the absorption spectrum of PTI-1 is very similar to that of fluorinated polymer PBDTTT-CF,⁵ which demonstrated a J_{sc} of 15 mA/cm² and a PCE of 7.4% in PSCs. Inspired by the favorable optical properties of PTI-1, we investigated the reasons for its relatively small J_{sc} . The atomic force microscopy (AFM) images of the blends of PTI-1:PC₇₁BM suggested too large domain size with sharp boundary may diminish charge generation and impede charge carrier transport in PSCs. It is known that PC₇₁BM has stronger absorption in visible region, but worse solubility than PC₆₁BM in most common organic solvents. The contribution of PC₇₁BM to J_{sc} in PTI-1 case may be not necessary because the second biggest absorption peak of PTI-1 overlaps with that of PC₇₁BM at 474 nm. Thus, the solubility and miscibility of the used acceptor with PTI-1 should be the first issue to be considered. In this letter, we will demonstrate that the J_{sc} and PCE of PSCs based on PTI-1:PC₆₁BM can reach 9.1 mA/cm² and 4.5%, respectively, due to the good solubility of PC₆₁BM and miscibility of the two components induced by DIO. Our results indicate that for PTI-1, PC₆₁BM is a better acceptor than PC₇₁BM despite its lesser absorption and slightly smaller driving force at the interface with PTI-1.²¹

The PSCs are fabricated in the configuration: Indium tin oxide (ITO)/PEDOT:PSS(40 nm)/PTI-1:PC₆₁BM/LiF (0.6 nm)/Al (80 nm). ITO covered glass substrates are first cleaned by detergent and acetone, then TL-1 (Ref. 12) treatment. PEDOT:PSS is spin-coated onto the cleaned substrate and baked for 20 min at 120 °C in ambient lab atmosphere. After that, the substrates are transferred into a glove box filled with N₂ atmosphere, where PTI-1:PC₆₁BM is spin-coated from o-dichlorobenzene (o-DCB) or o-DCB:DIO (2.5% vol. DIO in o-DCB) solution onto PEDOT:PSS with several spin-coating speeds. The thicknesses of all PSCs are

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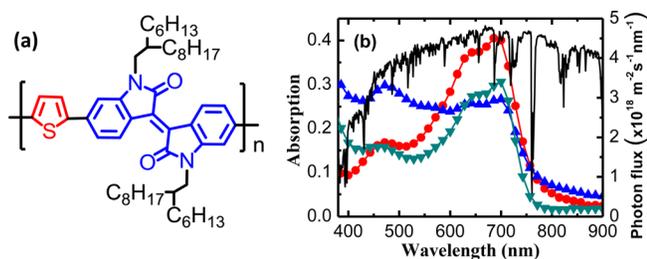


FIG. 1. (Color online) (a) The chemical structure of PTI-1, (b) the UV-vis absorption spectra of PTI-1 (circles), PTI-1:PC₇₁BM (up-triangles), and PTI-1:PC₆₁BM (down-triangles) from o-DCB:DIO as well as the solar photon flux (solid line).

optimized to approximately 80 nm. The top electrode LiF/Al is thermal evaporated at pressure less than 5×10^{-6} mbar. Device characterization has been carried out using the same setup as in Ref. 19 and in lab ambient environment without encapsulation. Films of PTI-1 and PTI-1:PCBMs (1:2) for absorption measurement are cast from o-DCB:DIO solutions on glass substrates. The external photoluminescence quantum efficiencies (PLQEs) are measured with an integrating sphere and calculated by the method proposed in Ref. 22.

The chemical structure of PTI-1 is given in Fig. 1(a) and the absorption spectra of PTI-1, the blends of PTI-1:PC₇₁BM, and PTI-1:PC₆₁BM cast from o-DCB:DIO together with a solar photon flux are shown in Fig. 1(b). The biggest absorption peak of PTI-1 matches well with the peak of solar photon flux. It is also obvious that the absorption intensity of PTI-1:PC₆₁BM are less than that of PTI-1:PC₇₁BM. In addition, the offset between LUMOs of PTI-1 and PC₆₁BM (0.16 eV) is smaller than that of PTI-1 and PC₇₁BM (0.25 eV),²¹ which may not be favorable for exciton dissociation. However, the two unfavorable factors of the blend PTI-1:PC₆₁BM do not limit the performance of the corresponding PSCs. The devices from the blends of PTI-1:PC₆₁BM in o-DCB with D/A ratio of 1:1 and 1:2 are fabricated and characterized. *J-V* characteristics and external quantum efficiencies (EQEs) are presented in Fig. 2. The performance parameters are summarized in Table I. As shown in Table I, discernible performance improvement of PSCs has been made by only changing the acceptor from PC₇₁BM to PC₆₁BM. J_{sc} is increased from 2.4 mA/cm² to 4.2 mA/cm² and from 3.1 mA/cm² to 3.5 mA/cm² for 1:1 and 1:2. The Fill Factor (FF) is slightly increased (0.49 to 0.50) for 1:1 and moderately increased (0.59 to 0.64) for 1:2. These result in PCE enhancement of 80% for 1:1 and 20% for 1:2, though V_{oc} is the same in both cases. The enhance-

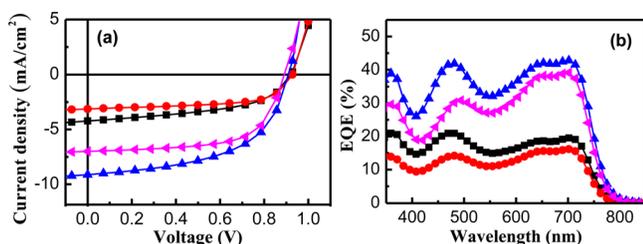


FIG. 2. (Color online) (a) the *J-V* and (b) EQEs of PTI-1:PC₆₁BM SCS with D/A ratio of 1:1 (squares) and 1:2 (circles) without DIO and 1:1 (up-triangles) and 1:2 with 2.5% DIO (left-triangles).

TABLE I. Performances of PSCs under illumination of 100 mW·cm⁻².

PTI-1:PC ₆₁ BM (wt. %)	DIO	J_{sc} (mA/cm ²)	FF	V_{oc} (V)	PCE (%)
1:1	No	4.2	0.50	0.92	2.0
	Yes	9.1	0.54	0.91	4.5
1:2	No	3.5	0.64	0.92	2.1
	Yes	7.0	0.66	0.89	4.2

ment of the performance from the blends of PTI-1:PC₆₁BM can be attributed to the improved morphology compared to the blends of PTI-1:PC₇₁BM due to better miscibility of PC₆₁BM, which encourages us to further modify the morphology with DIO as an additive.

The PSCs with stoichiometries of 1:1 and 1:2 are made from o-DCB:DIO (2.5% by volume) solution under the same processing conditions. The *J-V* characteristics and EQEs of the PSCs are depicted in Figs. 2(a) and 2(b), respectively. The performance parameters are also listed in Table I. Comparing the performance of PSCs based on PTI-1:PC₆₁BM with PTI-1:PC₇₁BM for stoichiometry 1:2, J_{sc} is increased from 5.4 mA/cm² to 7.0 mA/cm², FF is elevated from 0.63 to 0.66 and V_{oc} is left unchanged, which leads to an increase of PCE from 3.0% to 4.2%. The PCE enhancement induced by DIO is 76% for the PSCs based on PC₇₁BM and 103% for PSCs based on PC₆₁BM. More pronounced impact of DIO on PCE suggests that the morphology of the active layers is modified more by the presence of DIO in blends of PTI-1:PC₆₁BM than in the blends of PTI-1:PC₇₁BM. The enhancement becomes more pronounced with increasing of polymer fraction. The highest J_{sc} of 9.1 mA/cm² and PCE of 4.5% are realized in the PSCs with stoichiometry of 1:1.

To correlate performance of devices with morphologies of the active layers and to conduct a comparison between the two fullerene derivatives, the height and phase images of four solid films (1:1 and 1:2 from o-DCB or o-DCB:DIO) are recorded by tapping mode AFM and exhibited in Fig. 3. Figs. 3(a) and 3(b) shows that domain size increases with amount of PC₆₁BM in blends. The appearance of grains in the film of 1:2 cast from neat o-DCB (Fig. 3(b)) indicates

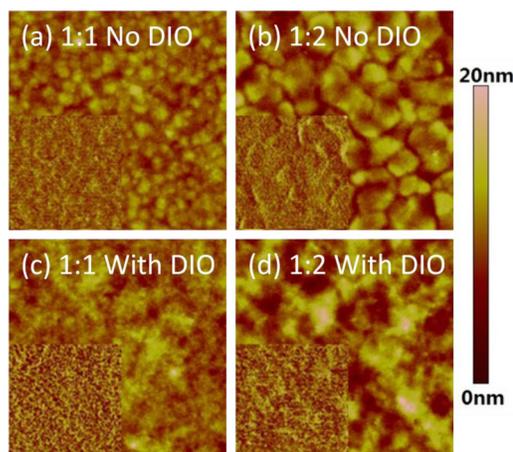


FIG. 3. (Color online) AFM height images and phase images (inset: 15°) ($2 \times 2 \mu\text{m}$) of PTI-1:PC₆₁BM films with ratio of 1:1 (a) and (c) and 1:2 (b) and (d) without DIO (a) and (b) and with DIO (c) and (d).

TABLE II. The PLQE of the films of PTI-1, PTI-1:PC₆₁BM (1:2), and PTI-1:PC₇₁BM (1:2) spin-coated from o-DCB or o-DCB:DIO.

Films	PTI-1	PTI-1	PTI-1:PC ₇₁ BM	PTI-1:PC ₇₁ BM	PTI-1:PC ₆₁ BM	PTI-1:PC ₆₁ BM
solvents	o-DCB	o-DCB:DIO	o-DCB	o-DCB:DIO	o-DCB	o-DCB:DIO
PLQE	0.47%	0.44%	0.09%	0.07%	0.14%	0.10%

strong phase separation between PTI-1 and PC₆₁BM. However, the roughness (RMS = 1.77 nm) is still smaller than that from its PTI-1:PC₇₁BM counterpart film (RMS = 2.40 nm).²⁰ Similar to the case of PTI-1:PC₇₁BM,²⁰ domains with sharp boundaries found in the films cast from pure o-DCB are replaced by blurred small domains in AFM images of the two films cast from o-DCB:DIO (Figs. 3(c) and 3(d)), which suggests that the miscibility between PTI-1 and PC₆₁BM is increased by using DIO as additive. This leads to a large interface for exciton dissociation and bi-continuous interpenetrating networks for free charge transportation, which is well consistent with the improved J_{sc} and FF in devices. The high performance corresponding to the fine morphology obtained in PSCs based on PC₆₁BM emphasizes the importance of the solubility and the morphology of active layers over the absorption in this specific case.

Moderate EQEs (about 40%) for the best devices may be the result of the small driving force or a two phase separated morphology, confirmed by incomplete PL quenching in the blends as listed in Table II. The PLQEs of PTI-1:PC₆₁BM is higher than those of PTI-1:PC₇₁BM, which is consistent with the smaller LUMO offset (0.16 eV) between PTI-1 and PC₆₁BM, compared to PC₇₁BM (0.25 eV) and indicates less efficient exciton dissociation in corresponding PSCs. However, higher J_{sc} and FF obtained from PTI-1:PC₆₁BM SCs suggests more efficient free charge carrier transport and collection. Furthermore, lower PLQEs of the films PTI-1:PC₆₁BM processed with DIO compared to those processed without DIO implies that the morphology of the active layer is indeed changed by DIO towards a positive way. The EQE of 40% might suggest that optimized morphology has not been achieved yet or that the driving force offset is indeed too small to have fully efficient exciton dissociation into free carriers. For this isoindigo-based polymer, exploring different processing conditions and tuning energy levels might reveal even higher PCEs.

In conclusion, we demonstrate that a 50% higher PCE is realized in the PSCs based on PTI-1:PC₆₁BM than PTI-1:PC₇₁BM even though the absorption of PC₆₁BM is less than that of PC₇₁BM. The performance enhancement is attributed to a more beneficial morphology of the PTI-1:PC₆₁BM active layer due to better solubility and miscibility of PC₆₁BM with PTI-1. Overall, the PCE of PSCs based

on PTI-1 can be increased from 3.0% to 4.5% by using PC₆₁BM instead of PC₇₁BM and DIO as additive. Since PL quenching is incomplete, further optimization of the device is possible, either by tuning morphology or energy levels.

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