

Fabrication and Characterization of PCBM: P3HT-based Thin-film Organic Solar Cells with Zinc Phthalocyanine and 1,8-Diiodooctane

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Abstract [6,6]-phenyl C₆₁-butyric acid methyl ester (PCBM) and poly(3-hexylthiophene) (P3HT) bulk heterojunction solar cells added with zinc-tetra-tertiary-butyl-phthalocyanine (ZnPc) and 1,8-diiodooctane (DIO) were fabricated and characterized. Incident photon-to-current conversion efficiencies in the range of 400–650 nm were increased by the ZnPc addition, and the absorption range of ZnPc overlapped with the photoluminescence range of P3HT. Photovoltaic properties of the solar cells with an inverted structure were improved by the ZnPc and DIO addition. Microstructures of the thin films were analyzed by X-ray diffraction. The improvement would be due to the Förster energy transfer mechanism the direct charge transfer from ZnPc to PCBM, and the phase separation of PCBM and P3HT by the DIO addition would also contribute the improvement.

Keywords Thin Film, Phthalocyanine, Solar Cell

1. Introduction

Organic thin-film solar cells have been developed as next-generation solar cell systems, and they have advantages of low cost, flexibility and light weight [1–3]. They can be fabricated at low temperatures by spin-coating and printing methods [4,5]. Polymer solar cells using poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl C₆₁-butyric acid methyl ester (PCBM) have been widely investigated, and the conversion efficiency of ~5 % was obtained [6,7]. Organic solar cells consisting of P3HT and PCBM exhibited good incident photon-to-current conversion efficiency (IPCE) and fill factor (FF). The device performance of such polymer solar cells can be affected by the preparation condition such as annealing

temperatures, concentration of starting materials and film thicknesses [8–10].

Addition of the third components such as phthalocyanines, naphthalocyanines and low-band-gap polymers is expected to absorb light that the P3HT and PCBM cannot collect. Since phthalocyanines absorb near-infrared light, effects of addition of silicon phthalocyanine, silicon naphthalocyanine or germanium phthalocyanine to the P3HT: PCBM system were investigated [11–17]. Solubilized metal phthalocyanines (MPc) could be dissolved in organic solvents, and the application for the device process using a spin-coating method could be expected.

MPc are groups of small molecular materials with Q-band absorption in the near-infrared ranges. Since they have high chemical stabilities and photovoltaic property, they can be used as donor materials for the organic solar cells. Heterojunction solar cells consisting of copper phthalocyanine and fullerene were fabricated by an evaporation method and their power conversion efficiencies was ~3% [18]. Characteristics such as absorption, conversion efficiencies and microstructures of thin film solar cells were investigated by changing the central metals of MPc [19–21].

The purpose of this work is to fabricate and characterize bulk heterojunction solar cells with an inverted structure using P3HT, PCBM and zinc-tetra-tertiary-butyl phthalocyanine (ZnPc). The ZnPc was added as the third component for PCBM: P3HT solar cells. 1,8-diiodooctane (DIO) was also added to improve the photovoltaic properties [22, 23]. The polarity of charge collection is reversed from conventional devices in the inverted structure [24–26], which are expected to provide stable devices in air [27–30]. The photovoltaic mechanism and an energy level diagram of the present solar cells were discussed on the basis of light-induced current density–voltage (J - V) curves and IPCE. The microstructures of thin films were investigated by X-ray diffraction (XRD).

2. Experimental Procedures

2.1. Materials

The molecular structures of organic semiconductor materials such as P3HT (Merck), ZnPc (Orient Chemical Industries), PCBM (American Dye Source), and DIO were used, as shown in Fig. 1(a), (b), (c) and (d), respectively. The TiO_x precursor solution was prepared from titanium isopropoxide (TTIP), and Indium tin oxide (ITO, Xin Yan Technology, $\sim 10 \Omega/\square$) was also used for substrates of the present photovoltaic devices.

2.2. Device Fabrication

Solar cells with an inverted structure were fabricated by the following process. ITO substrates were cleaned by an ultrasonic bath with acetone and methanol and dried with nitrogen gas. The TiO_x precursor solution was prepared from TTIP, 2-methoxyethanol, and acetylacetone. TTIP (0.5 mL) was added to 2-methoxyethanol (2.5 mL) and acetylacetone (0.422 mL) [15]. The TiO_x precursor solution was spin-coated on the ITO substrate at 2000 rpm. After annealing at 150 °C for 60 min in air, an organic layer was prepared on the TiO_x layer by spin coating at 1000 rpm using a mixed solution of P3HT (15 mg), PCBM (10 mg), and ZnPc in *o*-dichlorobenzene (1 mL). A weight ratio of ZnPc in PCBM:P3HT:ZnPc powders was changed 1, 3 and 5%. 1,8-diiodooctane was added 3 vol% in mixed solution of P3HT, PCBM and ZnPc. After annealing at 140 °C for 5 min in air, a PEDOT:PSS layer was spin-coated on the organic layer at 2000 rpm, and annealed at 100 °C for 5 min in air. Finally, gold (Au) metal contacts were evaporated as top electrodes. A solar cell without ZnPc was denoted as PCBM:P3HT. PCBM:P3HT solar cells added with 0 wt%, 1 wt%, 3 wt% and 5 wt% ZnPc were denoted as PCBM:P3HT, PCBM:P3HT(ZnPc1), PCBM:P3HT(ZnPc3) and PCBM:P3HT(ZnPc5), respectively. PCBM:P3HT solar cells added with 0 wt%, 1 wt%, 3 wt% and 5 wt% ZnPc and 3 vol% DIO were denoted as PCBM:P3HT-D, PCBM:P3HT(ZnPc1-D), PCBM:P3HT(ZnPc3-D) and PCBM:P3HT(ZnPc5-D), respectively. Layered structures of bulk heterojunction solar cells with the inverted structure were shown schematically in Fig. 2.

2.3 Characterization

The J - V characteristics (Hokuto Denko HSV-110) of the solar cells were measured both in the dark and under illumination at 100 mW cm^{-2} by using an AM 1.5 solar simulator (San-ei Electric XES-301S). The solar cells were illuminated through the side of the ITO substrates, and the illuminated area was 0.16 cm^2 . External quantum efficiencies (EQE) were also measured (Enli Technology, QE-R). Optical absorption of the solar cells was investigated by ultraviolet-vis-near-infrared spectrophotometer (Jasco, V-670ST). Photoluminescence

(PL) was investigated by spectrofluorometer (Jasco, FP-6600). Microstructures of the thin films were investigated by XRD analysis (Bruker, D2 Phaser) with Cu $K\alpha$ radiation. Crystallite sizes were calculated by Scherrer's equation.

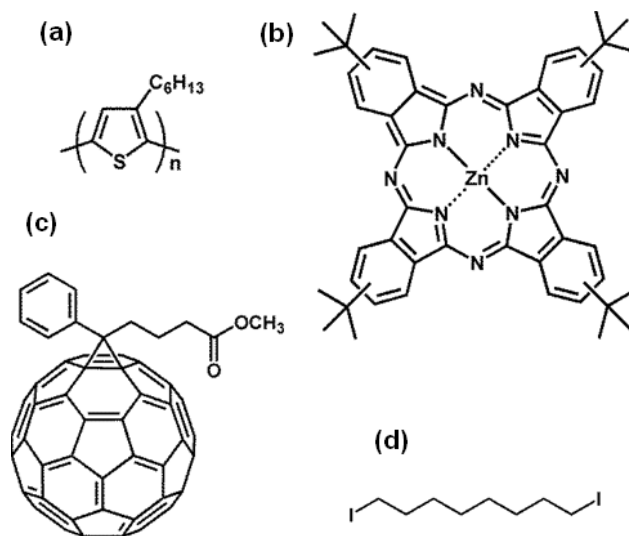


Figure 1. Structures of (a) P3HT, (b) ZnPc, (c) PCBM, and (d) DIO.

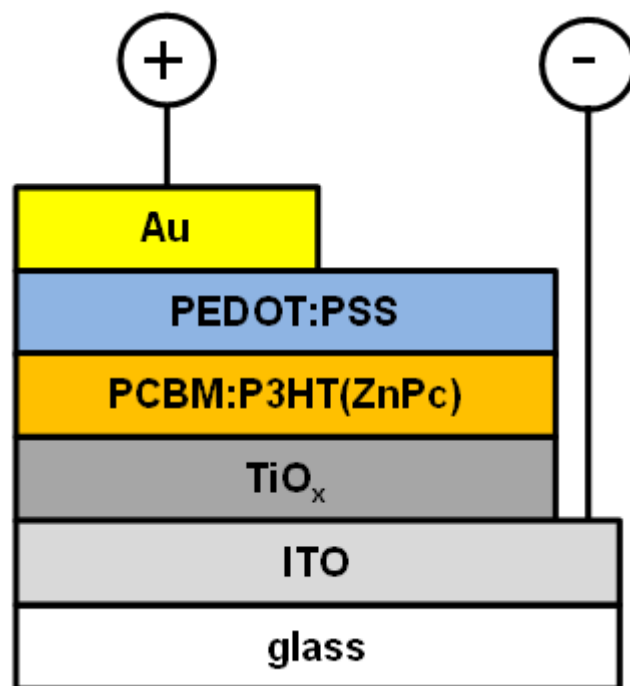


Figure 2. Schematic illustration of solar cell devices.

3. Results and Discussion

Figure 3 shows absorption spectra of PCBM:P3HT, PCBM:P3HT(ZnPc1), PCBM:P3HT(ZnPc3) and PCBM:P3HT(ZnPc5) and ZnPc thin films and a photoluminescence spectrum of a P3HT thin film. The absorption measurement region is in the range of 300–800 nm. Δ absorbance indicates the subtracted absorbance of

ITO/TiO_x. The optical absorption at 350 nm corresponds to the Soret band of ZnPc. The optical absorption in the range of 400–650 nm corresponded to P3HT, and absorption at ~400 nm was attributable to PCBM. The optical absorption in the range of 550–750 nm corresponds to the Q-band of ZnPc. The optical absorption range of PCBM:P3HT(ZnPc) film was expanded in the range of 400–750 nm by the ZnPc addition. The light with a wavelength of 460 nm was used for excitation of the P3HT, and a photoluminescence peak is observed at ~650 nm. The absorption range of ZnPc overlapped with the photoluminescence range of P3HT around 650 nm.

Measured parameters of PCBM:P3HT(ZnPc) solar cells are summarized in Table 1. Short-circuit current density, open-circuit voltage, fill factor and power conversion efficiency are denoted as J_{SC} , V_{OC} , FF and η , respectively. Figure 4 shows measured $J-V$ characteristic curves of the PCBM:P3HT(ZnPc) solar cells, and the J_{SC} was improved by the ZnPc addition. The PCBM:P3HT(ZnPc3) solar cell provided J_{SC} of 3.73 mA cm⁻² and η of 0.653 %, which were better than those of other PCBM:P3HT(ZnPc) devices in this work. The EQE spectra of solar cells are shown in Fig. 5. The EQE peaks were improved at ~730 nm for the solar cell with ZnPc, which is due to the optical absorption of the ZnPc. In addition, EQE were enhanced in the range of 300–650 nm. The enhancement would be stemmed from energy transfer mechanism by the ZnPc.

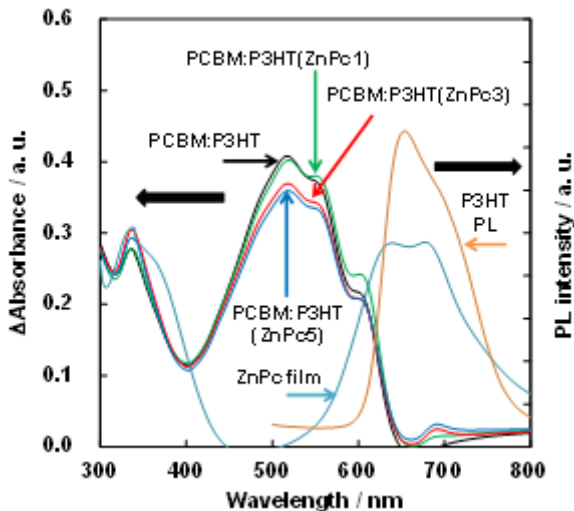


Figure 3. Optical absorption spectra of PCBM:P3HT(ZnPc), ZnPc thin films, and photoluminescence spectrum of P3HT thin film.

Table 1. Measured parameters of PCBM:P3HT(ZnPc) solar cells.

ZnPc (wt%)	J_{SC} (mA cm ⁻²)	V_{OC} (V)	FF	η (%)
0	3.41	0.452	0.403	0.621
1	3.56	0.424	0.408	0.615
3	3.73	0.435	0.403	0.653
5	3.56	0.422	0.398	0.597

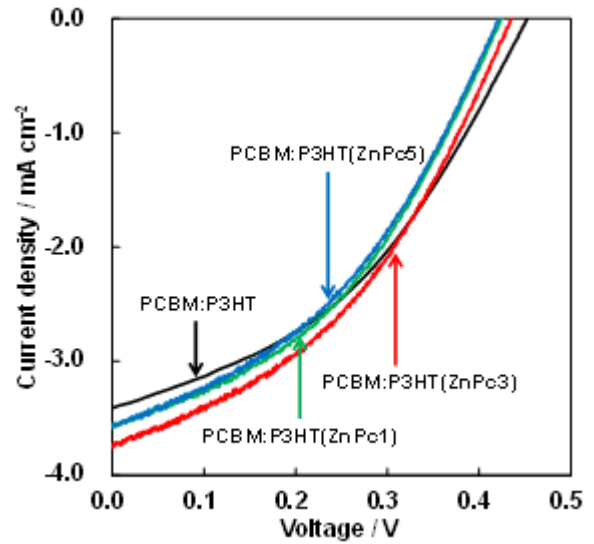


Figure 4. $J-V$ characteristics of PCBM:P3HT(ZnPc) solar cells.

Figure 6 shows absorption spectra of PCBM:P3HT(ZnPc) solar cells with DIO. Measurement region of the absorption is in the range of 300–800 nm. The optical absorption of P3HT in the range of 400–650 nm was slightly improved by the DIO addition. Absorption around 700 nm increased by the ZnPc addition compared with the PCBM:P3HT-D.

Measured parameters of the PCBM:P3HT(ZnPc) solar cells with DIO are summarized in Table 2. Figure 7 shows measured $J-V$ characteristic curves of PCBM:P3HT(ZnPc-D) solar cells. The J_{SC} of PCBM:P3HT with DIO was 4.67 mA cm⁻², which is higher than that of 3.41 mA cm⁻² for PCBM:P3HT cells. This indicates that the J_{SC} was improved by the DIO addition. However, J_{SC} of solar cells added with ZnPc and DIO were a little lower than that of solar cell without ZnPc. The ZnPc might prevent the phase separation by DIO addition.

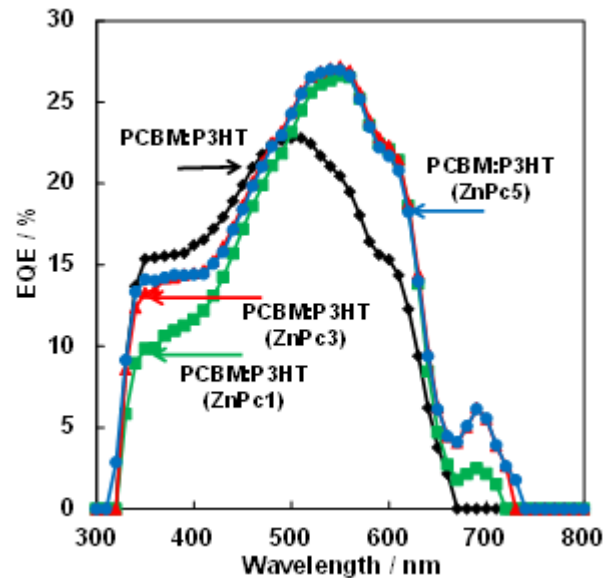


Figure 5. EQE spectra of PCBM:P3HT(ZnPc) solar cells.

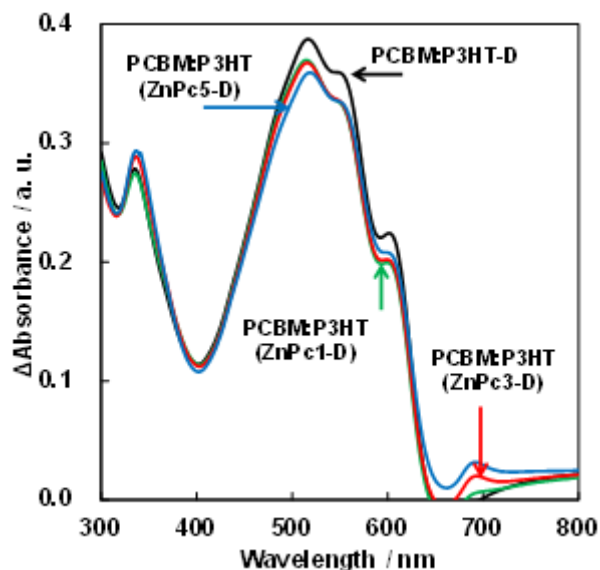


Figure 6. Optical absorption spectra of thin films of PCBM:P3HT(ZnPc) with DIO.

The EQE spectra of PCBM:P3HT(ZnPc-D) solar cells are shown in Fig. 8. The EQEs of all solar cells were improved by the DIO addition. Especially, PCBM:P3HT-D solar cell provided high EQE in the range of 450–650 nm. On the other hand, EQEs are observed at 700 nm by the ZnPc addition, and the values increased as the amount of ZnPc increased.

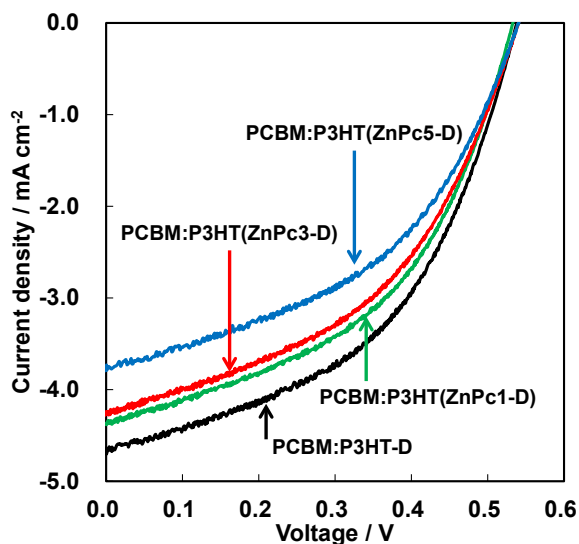


Figure 7. J - V characteristics of PCBM:P3HT(ZnPc) with DIO.

Table 2. Measured parameters of PCBM:P3HT(ZnPc) solar cells with DIO.

ZnPc (wt%)	J_{sc} (mA cm ⁻²)	V_{oc} (V)	FF	η (%)
0	4.67	0.539	0.483	1.21
1	4.37	0.533	0.475	1.11
3	4.27	0.539	0.458	1.06
5	3.79	0.540	0.458	0.936

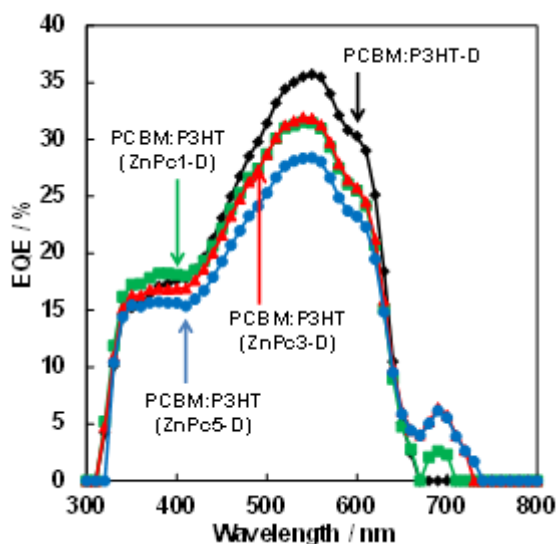


Figure 8. EQE spectra of PCBM:P3HT(ZnPc) with DIO.

XRD patterns of PCBM:P3HT, PCBM:P3HT(ZnPc), PCBM:P3HT-D and PCBM:P3HT(ZnPc-D) thin films are shown in Figure 9. Lattice parameters and crystallite sizes of PCBM:P3HT, PCBM:P3HT(ZnPc), PCBM:P3HT-D and PCBM:P3HT(ZnPc-D) thin films are summarized in Table 3. Diffraction peaks were observed for P3HT, PCBM:P3HT, PCBM:P3HT(ZnPc), PCBM:P3HT-D and PCBM:P3HT(ZnPc-D), which indicated that the P3HT have crystalline structures with lattice distances of 16.83, 16.41, 16.58, 16.55, and 16.58 Å, respectively. On the other hands, no sharp diffraction peak is observed for ZnPc and PCBM, which indicates that the ZnPc and PCBM has an amorphous structure. P3HT nanowires would be dispersed in the PCBM amorphous matrix, which had already been confirmed by XRD and transmission electron microscopy analyses in the previous work [15].

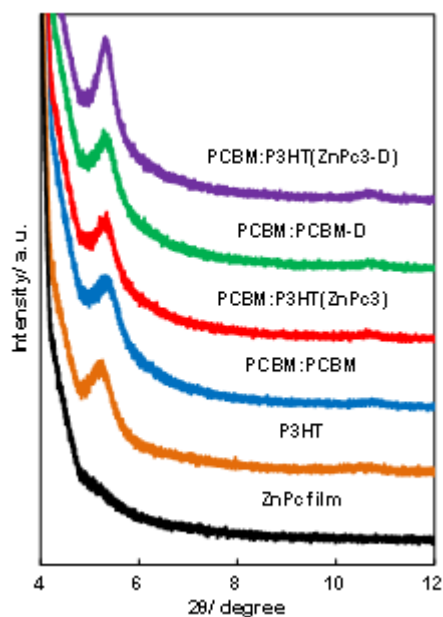
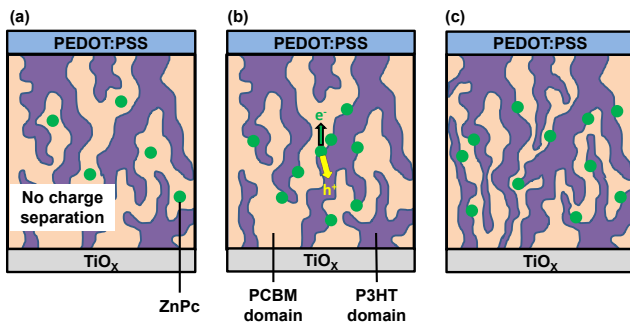
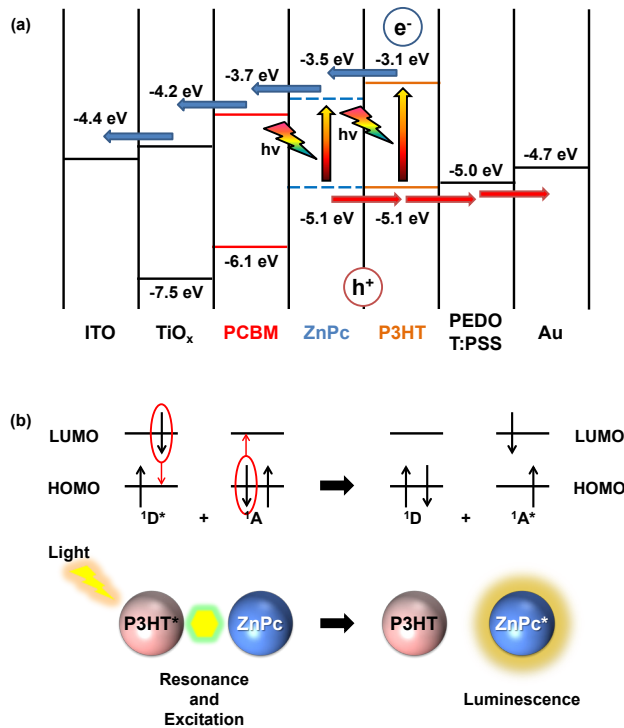


Figure 9. XRD patterns of thin films of ZnPc, P3HT, PCBM:P3HT, PCBM:P3HT(ZnPc), PCBM:P3HT-D, and PCBM:P3HT(ZnPc)-D.

Table 3. XRD results of the present thin films.

Sample	2θ ($^{\circ}$)	d -spacing (\AA)	Crystallite size (\AA)
P3HT	5.247	16.83	219
P3HT:PCBM	5.381	16.41	220
P3HT:PCBM(ZnPc)	5.327	16.58	244
P3HT:PCBM-D	5.335	16.55	290
P3HT:PCBM(ZnPc-D)	5.326	16.58	263

**Figure 10.** Schematic illustration of dispersion states of ZnPc (a) in PCBM matrix, (b) at the PCBM/P3HT interface and (c) with DIO.**Figure 11.** (a) Energy level diagram of PCBM:P3HT(ZnPc) solar cell. (b) Schematic illustration of Förster energy transfer mechanism.

Crystallite sizes of P3HT, PCBM:P3HT, PCBM:P3HT(ZnPc), PCBM:P3HT-D and PCBM:P3HT(ZnPc-D) were calculated to be 219, 220, 244, 290 and 263 \AA , respectively. The addition ZnPc and DIO facilitated the increase of the lattice parameters of P3HT crystalline. The crystallite size of PCBM:P3HT-D was the largest, and the solvent additive would facilitate the crystal growth and phase separation of PCBM:P3HT layers.

Interfacial structure models and an energy level diagram of the present PCBM:P3HT(ZnPc) solar cell are summarized and illustrated, as shown in Figures 10 and 11, referring the previous models and mechanisms [3,15-19]. If the ZnPc molecules exist in the PCBM domain, charge transfer does not occur, as shown in Fig. 10(a). Therefore, the EQE peaks of ZnPc would appear only when the ZnPc molecules exist at the PCBM:P3HT interface. When the ZnPc molecules exist at the PCBM:P3HT interface as illustrated in Fig. 10(b), photo-excitation would occur at the PCBM/ZnPc interface. When the DIO was added, the crystallite sizes of P3HT increased, which indicates the growth of the P3HT perpendicular to the substrate, as illustrated in Fig. 10(c). Then, the interfacial area increase, which resulted in the J_{SC} values.

For the cell with the inverted structure, electrons are transported to an ITO substrate, and holes are transported to an Au electrode, as illustrated in Fig. 11(a). Light irradiation promoted to generate charge separations. The excited electrons in the conduction band of the P3HT would slightly diffuse and transfer from P3HT to Au electrode. The holes in the valence band of the P3HT would pass through PEDOT:PSS layer to the ITO substrate. The energy levels of the conduction band or lowest unoccupied molecular orbital (LUMO) for P3HT, ZnPc and PCBM are -3.1 eV, -3.5 eV and -3.7 eV, respectively. Since the LUMO value of the ZnPc is between those of P3HT and PCBM, electrons could transport from P3HT to PCBM [16].

The EQE values in the range of 300–650 nm were increased by the ZnPc addition, which could be explained by the Förster energy transfer from the P3HT to ZnPc. Figure 11(b) shows Förster energy transfer mechanism, which occurs when the photoluminescence spectrum of a donor material and the photo-absorption spectrum of an acceptor material are overlapping [31,32]. In the present work, the donor and acceptor materials are P3HT and ZnPc, respectively. As shown in Fig. 3, the optical absorption spectra of ZnPc thin film and the photoluminescence spectrum of P3HT thin film are overlapping. Then, the Förster energy transfer would occur between the P3HT and ZnPc.

P3HT:PCBM with SiPc solar cells have also been studied recently [33-36], and the interface engineering for the ternary blend polymer solar cells were investigated and discussed in detail. In the present work, combination of the ternary blend polymers and DIO is an important point, and the microstructure model at the interface was proposed from XRD analysis and optical property measurements. Further optimization of the devices is mandatory to get higher performance in the future work.

4. Conclusions

PCBM: P3HT(ZnPc) bulk heterojunction solar cells with an inverted structure were fabricated and characterized. The

short-circuit current density of the solar cells were improved by the ZnPc addition. IPCE spectra of the PCBM:P3HT(ZnPc) solar cells showed peaks at 690 nm, and the IPCE intensities in the range of 400–650 nm were increased by the ZnPc addition. The absorption of the ZnPc was in the range of 550–800 nm, and the photoluminescence of P3HT was in the range of 600–800 nm. Since the absorption range of ZnPc overlapped with the photoluminescence range of P3HT, the Förster energy transfer from P3HT to ZnPc would occur. The increase in conversion efficiency of the PCBM: P3HT cells by the ZnPc addition would be explained in terms of the direct charge transfer from ZnPc to PCBM and the Förster energy transfer from P3HT to ZnPc. The Current density and efficiencies of PCBM:P3HT bulk heterojunction solar cells were also improved by the DIO addition, which would be due to the crystallite growth of the P3HT and phase separation of PCBM:P3HT layers.

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