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Efficiency enhancement in mesogenic-phthalocyanine-based solar cells with processing additives

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Bulk heterojunction (BHJ) solar cells, fabricated by spin casting processes, with phase-separated small molecules including a phthalocyanine derivative, 1,4,8,11,15,18,22,25-octaheptylphthalocyanine (C6PcH₂), and a fullerene derivative, 1-(3-methoxy-carbonyl)-propyl-1-phenyl-(6,6)C61 (PCBM), have been demonstrated to have a power conversion efficiency exceeding 4.1%. The C6PcH₂:PCBM BHJ surface morphology and the phase separation have been controlled by utilizing processing additives in various solvents. The effects of the processing additives on the crystallization of the discotic C6PcH₂ columns in hexagonal structures have been discussed. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4773519>]

Recently, organic solar cells (OSCs) have attracted considerable attention for the low-cost conversion of sunlight into electricity using lightweight and flexible cells.¹ In particular, bulk heterojunction (BHJ) solar cells have emerged as a promising technology because they can be manufactured by solution-based coating methods.^{2–4} Despite a continuing increase in the power conversion efficiency (PCE) of solar cells over the past few years, mostly due to the development of potential donor and acceptor materials,^{4–6} the relatively poor device performance of the cells remains a problem.

As a part of our efforts to synthesize potential donor materials, we have recently introduced a mesogenic phthalocyanine derivative, 1,4,8,11,15,18,22,25-octaheptylphthalocyanine (C6PcH₂), as a promising small molecule for use in BHJ solar cells.⁷ C6PcH₂ exhibits not only excellent processability for a thin film but also appropriate electronic characteristics for a solar cell, such as a deep highest occupied molecular orbital energy level, a relatively small band gap, strong optical absorption, and particularly high hole and electron drift mobilities exceeding 1.4 cm² V⁻¹ s⁻¹ and 0.5 cm² V⁻¹ s⁻¹ in the crystalline phase, respectively, which were evaluated by time-of-flight measurement. Despite their prominent characteristics, solar cells, the active layer of which was composed of C6PcH₂ and a fullerene derivative, 1-(3-methoxy-carbonyl)-propyl-1-phenyl-(6,6)C61 (PCBM), showed relatively low performance (PCE > 3%) owing to poor BHJ-separated phases.^{8,9}

Herein, we report the high performance of C6PcH₂:PCBM BHJ solar cells fabricated with separated phases. The BHJ nanomorphology and the separation of donor and acceptor phases were improved by using two different methods: (i) changing the solvents used and (ii) utilizing processing additives.

The molecular structure and energy level diagram of the small molecule C6PcH₂ are shown in Fig. 1. C6PcH₂ was

synthesized in accordance with the literature¹⁰ with slight modifications and fully purified by column chromatography (silica gel with toluene as the eluent), followed by repeated recrystallization from toluene-methanol (1:2) solution.⁷ PCBM was purchased from Frontier Carbon Ltd.

BHJ films were prepared under optimized conditions in accordance with the following procedure reported previously:¹¹ An indium tin oxide (ITO)-coated quartz substrate was cleaned with detergent, ultrasonicated in water, chloroform, acetone, and isopropyl alcohol, and subsequently treated with UV ozone. 6-nm-thick MoO_x films were thermally evaporated onto ITO substrates at a rate of 0.1 Å/s under a vacuum of about 2 × 10⁻⁶ Pa. After transferring to a N₂-filled glove box, a solution containing a mixture of C6PcH₂:PCBM

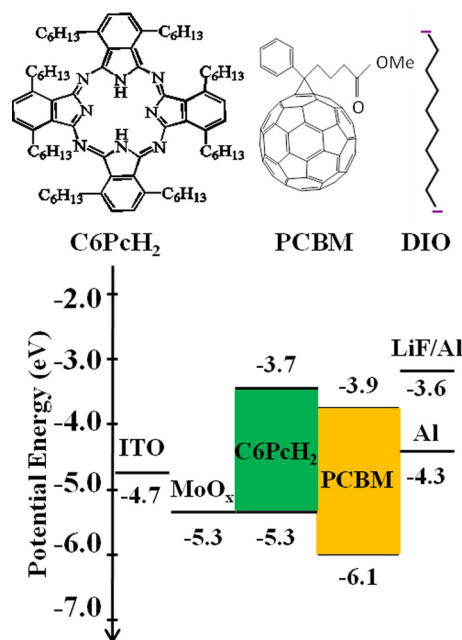


FIG. 1. Molecular structures of C6PcH₂, PCBM, and DIO and energy level diagrams of the solar cell in this study.

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(2:1) in various organic solvents, such as toluene, trichloroethylene (TCE), and chloroform with or without a 0.2% v/v 1,8-diiodooctane (DIO) solvent additive, was spin-cast onto the MoO_x layer. The thickness of the active layer was approximately 140 nm. Finally, a 0.3-nm-thick LiF buffer layer and 80-nm-thick aluminum films were deposited through a shadow mask by thermal evaporation under a vacuum of about 2×10^{-6} Pa. The active area of the device was 4 mm². The current density-voltage (J-V) characteristics were measured using a Keithley 236 source measure unit under the illumination of an XES 301 (AM 1.5 G) full spectrum solar simulator with an irradiation intensity of 100 mW/cm². Otherwise, the external quantum efficiency (EQE) spectra were measured with a programmable electrometer using a xenon lamp light passing through a monochromator used as a light source. The absorbance spectra and X-ray diffraction (XRD) patterns of the C6PcH₂:PCBM BHJ thin films were measured using a spectrophotometer (Shimadzu UV-3150) and an X-ray diffractometer (RINT 2000), respectively. The morphology of the thin films was observed by atomic force microscopy (AFM, Keyence VN-8000).

Figure 2 shows the absorbance spectra of the C6PcH₂:PCBM thin films fabricated on quartz substrates with and without the DIO solvent additive in toluene solution. The addition of DIO to the toluene solution induced a clear red shift of 2 nm at the Q-band and greater absorption at the B-band. Such a shift of the absorption peak to lower energies associated with the π - π^* transition when the films were processed with DIO indicated that the discotic C6PcH₂ columns in hexagonal structures interact more strongly and that there is an improvement in local structural order, compared with the case when the films were processed from pure toluene.^{12,13} The slight blue shift with the addition of PCBM to the C6PcH₂ thin films indicated the diffusion of PCBM into the discotic C6PcH₂ columns in hexagonal structures, as reported by Nekelson *et al.*¹⁴

As shown in Fig. 3(a), the C6PcH₂:PCBM devices without DIO in toluene showed a higher PCE of 3.1%, with a short-circuit current density (J_{sc}) of 7.4 mA/cm², an open-circuit voltage (V_{oc}) of 0.83 V, and a fill factor (FF) of 50%, than the devices fabricated using chloroform and TCE as solvents. By using processing additives to control the nanomorphology, the performance of BHJ solar cells was markedly improved. As depicted in Fig. 3(b), by adding 0.2% v/v DIO

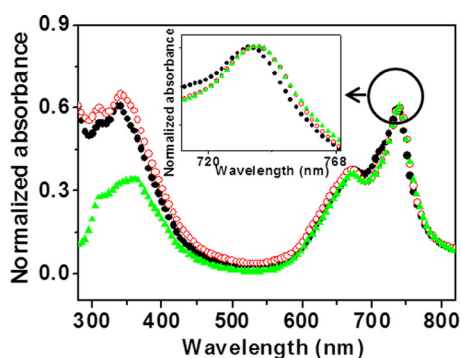


FIG. 2. Absorption spectra of the C6PcH₂ and PCBM composite thin films with (empty circles) and without (filled circles) DIO and the pristine C6PcH₂ (filled triangles).

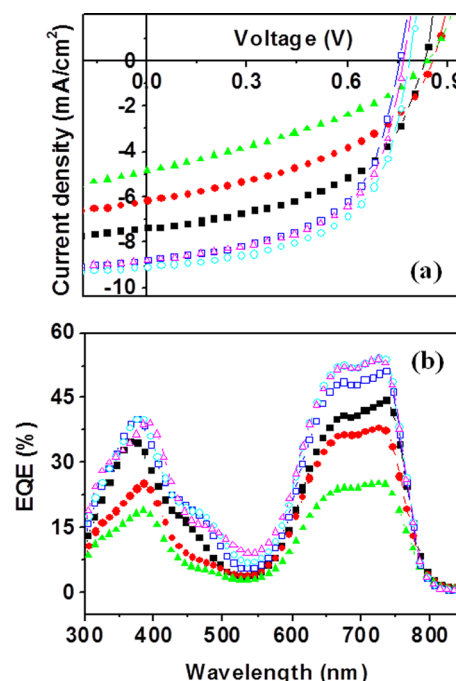


FIG. 3. J-V characteristics (a) and EQE spectra (b) of cells with DIO (empty symbols) and without DIO (filled symbols) in the various solvents: chloroform (triangles), TCE (circles), and toluene (rectangles).

to TCE, the EQE was improved from 38% to 54% at the Q-band and the shoulder of the B-band emerged at 450 nm, which were in good agreement with the results observed for the absorbance spectra. The dependence of the cell characteristics on the addition of DIO to the various solvents is shown in Table I. With the addition of 0.2% v/v DIO to TCE, J_{sc} and FF markedly increased to 9.1 mA/cm² and 58%, respectively. Together with a V_{oc} of 0.78 V, the PCE was estimated to be 4.1%.

The surface morphologies of C6PcH₂:PCBM composite films, with and without the incorporation of processing additives, which were observed by AFM, are shown in Fig. 4. On the smooth surface of the C6PcH₂:PCBM composite thin films, a number of islands, which are considered to be discotic C6PcH₂ domains, appeared with the incorporation of DIO as a processing additive. This suggests that utilizing DIO as a processing additive caused the separation of donor and acceptor phases. Moreover, the higher uniformity of the discotic C6PcH₂ domain islands on the C6PcH₂:PCBM composite thin films with TCE probably caused the higher PCE compared with the other films. These results imply that there is a relation between solvents for the optimum control of the nanomorphology, and hence the device performance of solar cells with C6PcH₂ and PCBM.

TABLE I. Characteristics of cells with and without DIO in different solvents.

Solvent	DIO	V_{oc} (V)	J_{sc} (mA/cm ²)	FF (%)	Efficiency (%)
Toluene	None	0.83	7.4	50	3.1
Toluene	0.2%	0.75	8.8	56	3.7
TCE	None	0.85	6.2	43	2.3
TCE	0.2%	0.78	9.1	58	4.1
Chloroform	None	0.84	4.8	37	1.5
Chloroform	0.2%	0.77	8.8	58	3.9

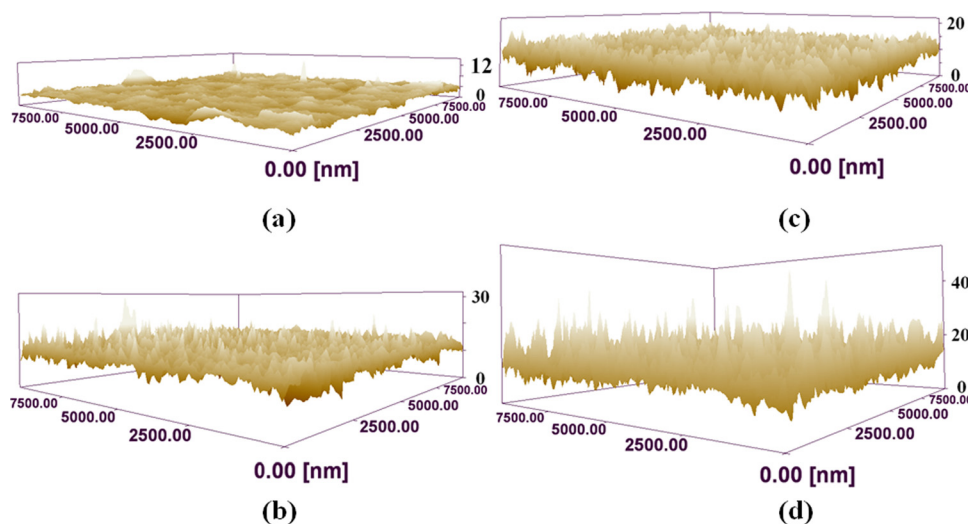


FIG. 4. AFM images of the C6PcH₂:PCBM thin films without DIO (a) and with DIO (b)–(d) in the various solvents: chloroform (a) and (b), TCE (c), and toluene (d).

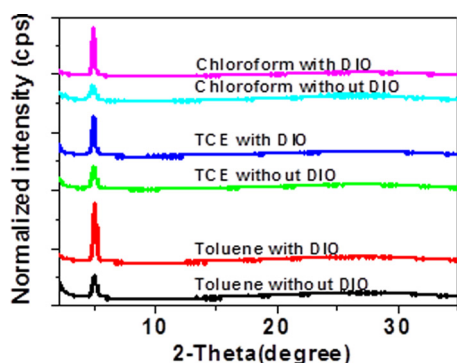


FIG. 5. XRD patterns of the C6PcH₂:PCBM thin films with and without DIO in different solvents.

Figure 5 shows the XRD patterns of C6PcH₂:PCBM thin films with and without DIO in various solvents. The decrease in the full width at half maximum of the XRD patterns upon adding DIO indicated the strong improvement of the crystallinity of the discotic C6PcH₂ columns in hexagonal structures. The strong dependence of the crystallization of the C6PcH₂ molecules on the addition of DIO is in complete contrast to previous reports indicating the absence of crystallization in films either with or without the processing additives.¹⁵ Although more effort should be made to understand the effects of the addition of DIO to C6PcH₂:PCBM BHJ, it is implied that the processing with DIO affects the separation of donor and acceptor phases, and that PCBM molecules aggregate. This reduces the diffusion of PCBM molecules into the discotic C6PcH₂ columns in hexagonal structures owing to the poor solubility of C6PcH₂ in DIO and the difference in boiling point between the processing additives and the main solvents.¹⁶

In summary, we reported significant improvements in the performance of BHJ solar cells based on C6PcH₂:PCBM upon changing the solvent used or incorporating processing additives to the solution. By adding 0.2% of DIO processing additive, the PCE of the device was improved from 2.3% to 4.1%. The surface morphology of C6PcH₂:PCBM thin films, as observed by AFM, exhibited C6PcH₂ domains, therefore, the processing additives separated the donor and acceptor

phases. Furthermore, the improvement of the crystallization of the discotic C6PcH₂ columns in hexagonal structures by adding DIO to solvents might be due to the aggregation of PCBM molecules, which reduces the diffusion of PCBM molecules into the discotic C6PcH₂ columns in the hexagonal structures.

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