



Original Article

Fabrication of Organic Solar Cell Utilizing Mixture of Solution-processable Phthalocyanine and Fullerene Derivative with Processing Additive Solvent

Quang-Duy Dao *

Faculty of Physics, VNU University of Science, 334 Nguyen Trai, Thanh Xuan, Hanoi, Vietnam

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Abstract: We demonstrate an efficient bulk heterojunction (BHJ) organic solar cell (OSCs) utilizing a soluble phthalocyanine derivative, 1,4,8,11,15,18,22,25-octaethylphthalocyanine (C6PcH₂), and a fullerene derivative, 1-(3-methoxy-carbonyl)-propyl-1-1-phenyl-(6,6)C71 and roles of processing additive solvent on improvement of the BHJ OSCs. By adding processing additive solvent, filling factor and short-circuit current density are improved to 0.57 and 8.6 mA/cm², respectively. As a result, the power conversion efficiency of 3.6% is achieved. Otherwise, the effects of processing additive solvent are demonstrated by taking the absorption and photoluminescence spectra of C6PcH₂ and composite thin films into account.

Keywords: Phthalocyanine, organic solar cells, thin film, small molecule, processing additive.

1. Introduction

Organic solar cells (OSCs) utilizing solution-processable small-molecule (SM) donors mixed with fullerene derivative have considered as an alternative to OSCs based on the conventional conjugated polymers [1-6]. Comparing with polymer-based donors, SM-based donors expose the dominant characteristics, such as relatively high charge carrier mobility, well-defined structures without end group contaminants, and simple synthesis and purification. OSCs based on SM donors in both of conventional and inverted structures have exhibited the relatively high photovoltaic performance with the power conversion efficiencies (PCEs) exceeding 10% [1].

*Corresponding author.

Email address: daoquangduy@hus.edu.vn

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Discotic liquid crystalline (DLC) materials have been reported as potential SM donors in bulk heterojunction (BHJ) OSC field [7-9]. DLC materials exhibit the appealing characteristics, such as the strong optical absorption at visible-light ranges, the large exciton diffusion length, and the relatively high charge carrier mobility [8]. Furthermore, the high solubility in conventional organic solvents and the strong self-organizing nature which leads to relatively easy fabrication of high quality thin films with large areas of mono-domain have made DLC materials more suitable for BHJ OSC application [10-14]. In this study, we demonstrate the relatively high photovoltaic performance OSCs utilizing non-peripherally substituted octahexyl phthalocyanine (C6PcH₂) (Fig. 1(a)) SM donor mixed with a fullerene derivative, 1-(3-methoxy-carbonyl)-propyl-1-1-phenyl-(6,6)C71 (PC₇₀BM) and the effects of processing additive on the device photovoltaic performance.

2. Experimental Procedure

2.1. Sample and device fabrication

BHJ OSCs, which had the device architecture as shown in Fig. 1(b), were prepared under optimized conditions in accordance with the previous literature [10]. In particular, indium tin oxide (ITO)-coated glass was patterned by wet-etching method using hydrochloric acid at 40 °C. The patterned ITO-coated glasses were then cleaned with detergent, water, chloroform, acetone, and isopropyl alcohol. In sequence, the ITO substrates were treated with UV-induced ozone to remove the redundant organic solvents. After that, MoO_x films were thermally evaporated onto the patterned-ITO substrates at a rate of 0.1 Å/s under a vacuum of about 2×10⁻⁵ Pa. The thickness of MoO_x film was around 6 nm. A solution containing a mixture of C6PcH₂ and PC₇₀BM (2:1) in chloroform at a total solids concentration of 22.35 mg/ml was then spin coated on the top of MoO_x layers in a N₂-filled glove box. The thickness of C6PcH₂ and PC₇₀BM BHJ layer was around 150 nm. To improve the nano-scale phase separation of donor and acceptor as well the photovoltaic performance of C6PcH₂-based devices, various amount of 1,8-diiodooctane (DIO, as shown in Fig. 1(b)) was added as a processing additive solvent [11]. Finally, 80-nm-thick aluminum and 3-nm-thick LiF films were thermally deposited at a rate of 3 and 0.1 Å/s under a vacuum of about 2 × 10⁻⁵ Pa, respectively. The device area was 4 mm².

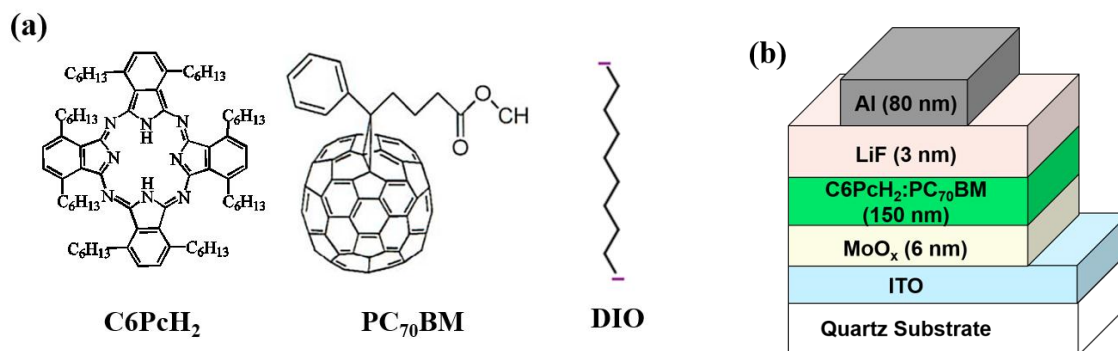


Figure 1. (a) Chemical structure of materials and (b) device architecture in this study.

C6PcH₂ was synthesized in accordance with the literature with slight modifications as following procedures [8, 15]. In particular, C6PcH₂ SM was fully purified by column chromatography (silica gel with toluene as the eluent) and repeatedly recrystallized from toluene-methanol (3:1) solution. PC₇₀BM (Frontier carbon Ltd.) and DIO (Sigma Aldrich) was used without further purification.

2.2. Film and device characterization

The current density-voltage (J - V) characteristics were measured using a source measurement unit (Keithley 2400) under 1-sun condition (using an XES 301 (AM 1.5 G) full spectrum solar simulator with the irradiation intensity of 100 mW/cm^2). The external quantum efficiency (EQE) spectra were measured using a xenon lamp light passing through a mono-chromator as a light source. The measurement system was calibrated using Si reference cells. The measured J - V characteristics show good agreements with the integrated EQE values. While the active-layer thickness was directly measured using atomic force microscopy (AFM, Keyence VN-8000), the thickness of LiF and MoO_x thin films was measured using thickness sensor, which inserted in vacuum chamber of with thermal evaporation system. We note that the thickness sensor in this study has been calibrated using AFM. The absorption and photoluminescence (PL) spectra of the C6PcH_2 : PC_{70}BM BHJ thin films were measured by spectrophotometry (Shimadzu UV-3150) and fluorescence spectrophotometer (Hitachi F-4500), respectively.

3. Results and discussion

Figure 2 shows the normalized absorption spectra of C6PcH_2 , PC_{70}BM , and C6PcH_2 : PC_{70}BM composites in solid thin films, fabricated on glass substrates. The absorption spectra of the C6PcH_2 SM donor exhibited the strong peaks at around 408 and 700 nm, related to allowed B transition and forbidden Q transition of porphyrinoid complexes, respectively [16, 17]. However, the absorption intensity at around 500 nm was quite low. By mixing C6PcH_2 SM donor with PC_{70}BM acceptor, the absorption intensity at round 500 nm was improved due to the absorption of PC_{70}BM molecules. As a result, the absorption of C6PcH_2 : PC_{70}BM composite thin film covered all visible spectral range.

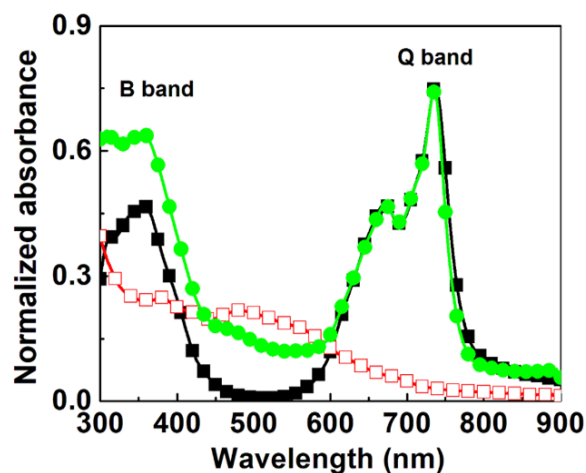


Figure 2. Absorption spectra of C6PcH_2 (filled-rectangles), PC_{70}BM (empty-rectangles), and C6PcH_2 : PC_{70}BM composite (filled-circles) thin films.

Figures 3(a) shows the EQE spectra of the BHJ OSCs on glass substrates utilizing C6PcH_2 SM donor mixed with PC_{70}BM acceptor with various amount of DIO processing additive solvent. The devices utilizing C6PcH_2 : PC_{70}BM composite thin films without DIO processing additive solvent exhibited broad EQE curves throughout the visible region, with the three predominated peaks at around 700, 400 and 500 nm. The shape of EQE curve was good agreement with the aforementioned absorption spectra

of the C6PcH₂:PC₇₀BM composite thin films. However, the EQE was relatively poor with the intensity of 8% at 700 nm due to the poor nano-scale donor-acceptor separation in the composite thin films [11]. By adding DIO processing additive solvent, the EQE of the OSC utilizing C6PcH₂:PC₇₀BM composite thin film was markedly improved. Particularly, the EQE intensity at 730 nm was improved to 43% by adding 0.2 %v/v of DIO processing additive solvent. We suggested that by adding the processing additive solvent, the nano-scale donor-acceptor phase separation of the C6PcH₂:PC₇₀BM composite thin film was improved, which caused the improvement in the device photovoltaic performance. However, the EQE intensity of the fabricated devices was reduced by adding 0.3 %v/v of DIO processing additive solvent.

Figure 3(b) shows the *J-V* characteristics of BHJ OSCs on glass substrates utilizing C6PcH₂ SM donors mixed with PC₇₀BM acceptors with various amount of the DIO processing additive solvent, under AM 1.5 G illumination at an intensity of 100 mW/cm². The all device data are summarized in Table 1. The devices based the C6PcH₂ SM donor without the DIO processing additive solvent exhibited the relatively poor *J-V* characteristics with the short-circuit current density (J_{sc}) of 1.6 mA/cm² and the open-circuit voltage (V_{oc}) of 0.81 V. With the filling factor (*FF*) of 0.27, the PCEs of 0.4 % were achieved. By using DIO processing additive solvent, the photovoltaic performance of the BHJ OSC was markedly improved. In particular, the J_{sc} and *FF* of the fabricated devices were improved to 8.6 mA/cm² and 0.57, respectively. As a result, the PCE of 3.6% was achieved. Although the PCE of BHJ OSC utilizing C6PcH₂ mixed with PC₇₀BM was still relatively low comparing with those of BHJ OSC utilizing benzodithiophene SM due to the low highest occupied molecular orbital energy levels of C6PcH₂ SM and/or the simple architecture of cell in this study, those results indicated that C6PcH₂ SM could be a potential donor in BHJ OSC [1]. On the other hand, the PCE of the fabricated devices was reduced to 1.8 % when 0.3 %v/v DIO was added to the mixture of C6PcH₂:PC₇₀BM solution. Those results were quite good agreement with the aforementioned EQE spectra of the device utilizing the C6PcH₂:PC₇₀BM composite thin films.

The PL spectra of C6PcH₂ and C6PcH₂:PC₇₀BM thin films fabricated on glass substrates with various DIO processing-additive solvent are shown in Fig. 4. The PL spectra of C6PcH₂ thin films had a shoulder at around 820 nm and a strong peak at 766 nm, related to the Q-band of the C6PcH₂ absorption spectra. The PL intensity of the C6PcH₂ SM donors was markedly suppressed by adding the PC₇₀BM acceptors. Those results indicated that the photo-induced electrons transfer from the excited state of C6PcH₂ to PC₇₀BM [18-20]. However, the PL intensity of C6PcH₂:PC₇₀BM thin films was increased by adding DIO processing-additive solvent. The increases in the PL intensity indicated that the interfacial areas between the donor and acceptor were enlarged or the nano-scale donor-acceptor phase separation was improved by adding DIO processing additive solvent, which was in good agreement with the aforementioned increases in the J_{sc} and PCE of the fabricated devices [11, 13, 14].

Table 1. OSCs utilizing C6PcH₂: PC₇₀BM BHJ thin film with various amounts of DIO processing additive solvent

Amount of DIO (% v/v)	V_{oc} (V)	J_{sc} (mA/cm ²)	<i>FF</i> (%)	PCE (%)
0	0.81	1.6	0.27	0.4
0.1	0.77	7.0	0.38	2.1
0.2	0.74	8.6	0.57	3.6
0.25	0.73	8.3	0.53	3.2
0.3	0.74	5.5	0.44	1.8

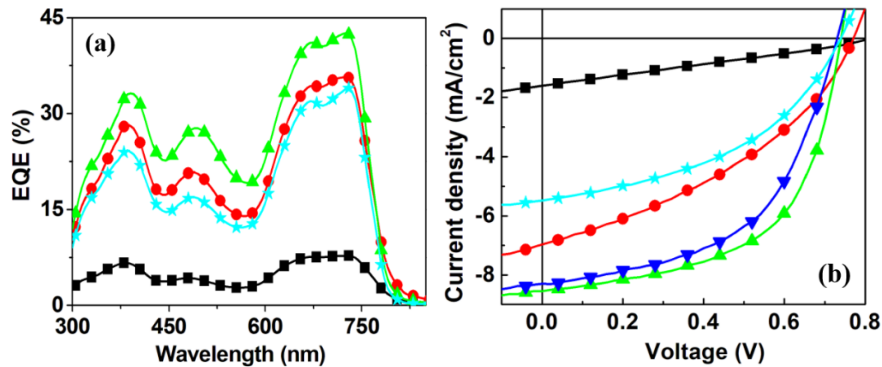


Figure 3. (a) EQE spectra and (b) J - V characteristics of OSCs utilizing C6PcH₂:PC₇₀BM BHJ thin film with various amounts of DIO processing additive solvent: 0 (rectangles), 0.1 (circles), 0.2 (up-triangles), 0.25 (down-triangles), and 3 (stars) %v/v.

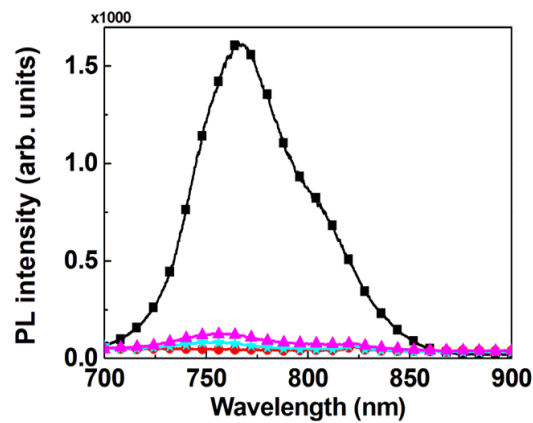


Figure 4. PL spectra of C6PcH₂ (rectangles) and C6PcH₂:PC₇₀BM BHJ thin film with various amounts of DIO processing additive solvent: 0 (circles), 0.25 (stars), and 3 (up-triangles) %v/v.

Figure 5(a) shows the absorption spectra at the Q band of the C6PcH₂ and C6PcH₂:PC₇₀BM composite in solution and solid thin films. It indicated that the width of the Q band was changed by adding PC₇₀BM and/or DIO processing additive solvent. Figure 5(b) shows the Davydov splitting at the Q band or the width of Q band of the C6PcH₂ and C6PcH₂:PC₇₀BM composite in solution and solid thin films. We note that the width of the Davydov splitting at Q band of phthalocyanine molecules is related to the interaction energy between discotic C6PcH₂ with different site symmetries. In particular, the increases in the Davydov splitting at Q band suggest that the molecular interaction of C6PcH₂ molecules was reinforced. As shown in Fig. 5(b), the Davydov splitting at Q band increased and molecular interaction of C6PcH₂ molecules was reinforced after removing the solvent. On the other hand, the Davydov splitting at Q band decreased by adding PC₇₀BM acceptor. Those results suggest that the dispersion of PC₇₀BM molecules into the C6PcH₂ domains was occurred and weakened the molecular interaction of discotic C6PcH₂. However, by adding the DIO processing additive solvent, the Davydov splitting at Q band increased again. We suggest that the doping DIO processing additive solvent separated the phase of C6PcH₂ donors and PC₇₀BM acceptors, which was in good agreement with the aforementioned improvement of the BHJ OSCs utilizing the C6PcH₂:PC₇₀BM composites thin films [11, 13, 14].

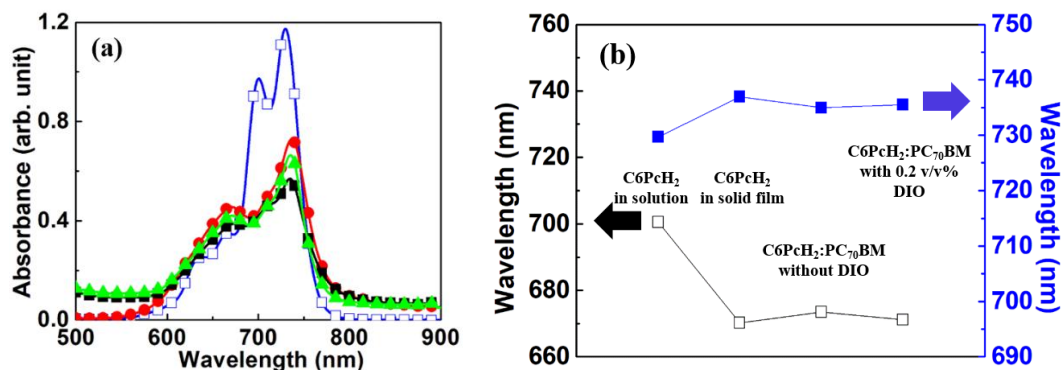


Figure 5. (a) Absorption spectra C6PcH₂ in chloroform solution (empty-rectangles) and solid thin films (filled-circles) and absorption spectra of C6PcH₂:PC₇₀BM BHJ thin film with various amounts of DIO processing additive solvent: 0 (filled-rectangles) and 2 (up-triangles) % v/v and (b) dependence of size of the Davydov splitting of C6PcH₂ and C6PcH₂:PC₇₀BM BHJ thin film.

4. Conclusions

In summary, an efficient BHJ OSC in ITO/MoO_x/C6PcH₂:PC₇₀BM /Al structure was fabricated with the relatively high photovoltaic performance. Furthermore, the roles of the DIO processing additive solvent on the photovoltaic performance of BHJ OSCs utilizing C6PcH₂:PC₇₀BM composite thin films was taken into account. Particularly, by adding 0.2 % v/v of DIO processing additive solvent, the nano-scale donor-acceptor phase separation was improved and the EQE at the Q band of BHJ OSC utilizing C6PcH₂:PC₇₀BM composite thin films increased from 8 to 43%. Hence, the J_{sc} and FF were markedly improved to 8.6 mA/cm² and 0.57, respectively. Finally, the PCE of 3.6% was achieved.

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