

Doping Effects of Liquid Crystalline Phthalocyanine in Bulk Heterojunction Polymer Solar Cells

Testuya Masuda¹, Tetsuro Hori¹, Naoki Fukuoka¹, Yasuo Miyake^{1,2}, Dao Quang Duy¹, Takeshi Hayashi¹, Toshiya Kamikado¹, Hiroyuki Yoshida¹, Akihiko Fujii¹, Yo Shimizu², Masanori Ozaki¹

¹ Division of Electrical, Electronic and Information Engineering, Graduate School of Engineering, Osaka University, 2-1 Yamada-oka, Suita, Osaka 565-0871, Japan
Phone: +81-6-6879-4837 E-mail: tmasuda@opal.eei.eng.osaka-u.ac.jp

² Research Institute for Ubiquitous Energy Devices, National Institute of Advanced Industrial Science and Technology (AIST), 1-8-31 Midorigaoka, Ikeda, Osaka 563-8577, Japan

1. Introduction

Poly(3-hexylthiophene) (P3HT) is known as one of the conventional active layer materials used in organic thin-film solar cells. However, the photoabsorption of P3HT is limited to the visible region at wavelengths shorter than 600 nm. Therefore, the improvement of long-wavelength sensitivity is important.

Recently, we have demonstrated high hole and electron drift mobilities of $1.4 \text{ cm}^2/\text{Vs}$ and $0.5 \text{ cm}^2/\text{Vs}$, respectively, in the crystalline phase of mesogenic non-peripheral octahexylphthalocyanine (C6PcH₂, shown in Fig. 1)^[1]. C6PcH₂ exhibits high absorption in the wavelength range of 600-800 nm corresponding to the Q-band, and C6PcH₂ forms a hexagonal columnar structure owing to its high self-organization and π -stacking properties. We also reported a simple organic solar cell with a bulk heterojunction of C6PcH₂ and fullerene derivative (PCBM) that was fabricated by the spin-coating method and demonstrated its high energy conversion efficiency^[2,3].

In this study, we report on the improvement of long-wavelength sensitivity in P3HT:PCBM bulk heterojunction solar cells by doping C6PcH₂ and discuss their photovoltaic properties by taking the microphase separation and photoinduced charge separation into consideration

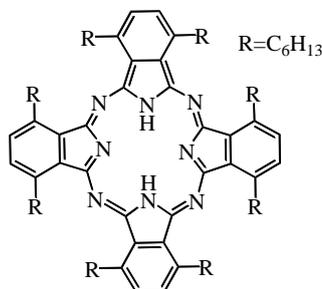


Fig. 1 Molecular structure of C6PcH₂

2. Experimental Details

The fabrication of solar cells in this study was carried out in the following manner. A hole transport layer of poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate)

(PEDOT:PSS) was spin-coated onto an indium-tin-oxide (ITO)-coated quartz substrate, and dried in an oven under atmospheric conditions. P3HT, C6PcH₂, PCBM were dissolved in chloroform. The P3HT:C6PcH₂:PCBM mixed solution was spin-coated onto the PEDOT:PSS layer in a glove box filled with argon gas.

Lithium fluoride (LiF) and aluminum (Al) layers as a counter electrode to the ITO were deposited onto the composite layer through shadow masks by thermal evaporation.

3. Results and Discussion

Figure 2 shows the external quantum efficiency (EQE) spectra of the solar cells with P3HT:PCBM and P3HT:C6PcH₂:PCBM active layers, the composition ratios of which were 1:1 and 10:3:10, respectively. In the solar cell without C6PcH₂, although a high EQE of 74% was obtained at the wavelength of 540 nm, corresponding to the absorption peak of P3HT, a low EQE was obtained at wavelengths longer than 650 nm because of the low absorbance of the active layer. On the other hand, in the solar cell with C6PcH₂, a high EQE of 46% at 730 nm originating from the absorption of C6PcH₂ was obtained as well as a high EQE of 66% at 540 nm. That is, the photosensitivity of the bulk heterojunction organic solar cell with the P3HT:PCBM active layer was improved in the near-infrared region.

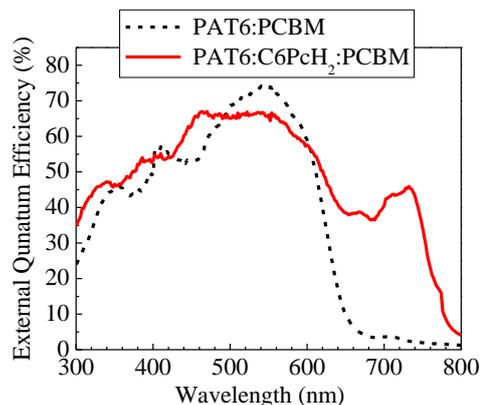


Fig. 2 EQE spectra of the solar cells with PAT6:PCBM and PAT6:C6PcH₂:PCBM active layers

Figure 3 shows typical current-voltage characteristics of the solar cells with active layers of P3HT:PCBM and P3HT:C6PcH₂:PCBM, the composition ratios of which were 1:1 and 10:3:10, respectively, under AM1.5G (100 mW/cm²) solar-illuminated conditions. Open-circuit voltage (V_{oc}) was mostly unchanged, and Fill Factor (FF) decreased. On the other hand, short-circuit current density (I_{sc}) was 1.4 times higher than in the case without C6PcH₂. The long-wavelength sensitivity in the EQE spectrum, as shown in Fig. 2, was improved by doping C6PcH₂, resulting in the enhancement of I_{sc} . The energy conversion efficiency of the solar cell without C6PcH₂ was 2.3% with V_{oc} of 0.56 V, I_{sc} of 8.6 mA/cm² and FF of 0.48, and that of the solar cell containing C6PcH₂ was improved to 3.0% with V_{oc} of 0.56 V, I_{sc} of 12.1 mA/cm² and FF of 0.44^[4].

Figure 4 shows the X-ray diffraction (XRD) patterns of bulk heterojunction active layers of P3HT:PCBM and P3HT:C6PcH₂:PCBM, the composition ratios of which were 1:1 and 10:3:10, respectively. The diffraction peak around $2\theta = 5.4^\circ$ corresponds to the distance of the main chain of P3HT (16.3 Å), and that around $2\theta = 4.9^\circ$ corresponds to the distance of the hexagonal column of C6PcH₂ (18.0 Å). At the P3HT:C6PcH₂:PCBM, the diffraction of C6PcH₂ appeared, although the diffraction intensity of P3HT was maintained. Therefore, it is considered that both P3HT and C6PcH₂ aggregate to form mutual microphase separation and that highly ordered P3HT domains and hexagonal columnar structures of C6PcH₂ coexist in the P3HT:C6PcH₂:PCBM bulk heterojunction thin film.

4. Conclusions

We reported on the improvement of the long-wavelength sensitivity in P3HT:PCBM bulk heterojunction organic thin-film solar cells by the doping of C6PcH₂, which is a liquid crystalline phthalocyanine derivative exhibiting near-infrared absorption, into the P3HT:PCBM bulk heterojunction active layer. At the composition ratio of P3HT:C6PcH₂:PCBM = 10:3:10, the photosensitivity in the wavelength region from 650 to 800 nm was improved, and I_{sc} was enhanced from 8.6 to 12.1 mA/cm². As a result, the energy conversion efficiency was improved from 2.3 to 3.0%. It was found that the bulk heterojunction was composed of both highly ordered P3HT domains and hexagonal columnar structures of C6PcH₂ at the P3HT:C6PcH₂ composition ratio of 10:3 and that P3HT and C6PcH₂ underwent mutual microphase separation in the active layer. We discussed the mechanisms of photoconversion in the bulk heterojunction organic thin-film solar cell based on the P3HT:C6PcH₂:PCBM active layer.

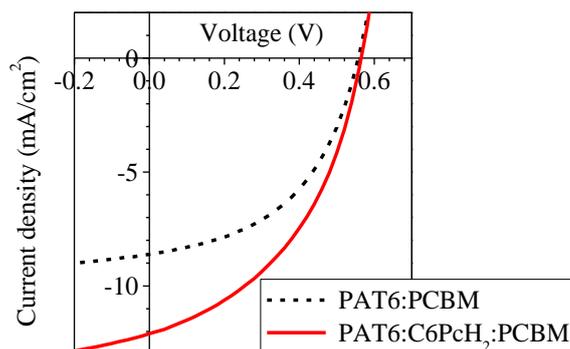


Fig. 3 Current density-voltage characteristics of the solar cells with PAT6:PCBM and PAT6:C6PcH₂:PCBM active layers under AM1.5G solar-illumination

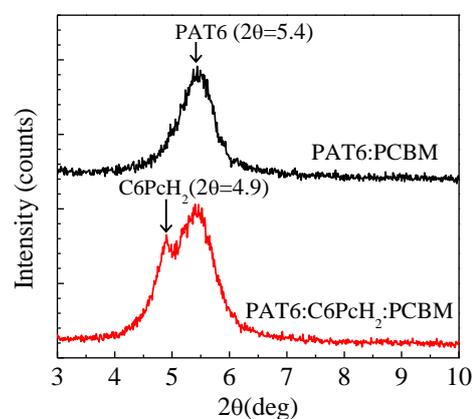


Fig. 4 XRD patterns of the bulk heterojunction active layers

References

- [1] Y. Miyake, Y. Shiraiwa, K. Okada, H. Monobe, T. Hori, N. Yamasaki, H. Yoshida, M. J. Cook, A. Fujii, M. Ozaki, and Y. Shimizu: *Appl. Phys. Express* **4** (2011) 021604.
- [2] T. Hori, Y. Miyake, N. Yamasaki, H. Yoshida, A. Fujii, Y. Shimizu, and M. Ozaki, *Appl. Phys. Express* **3** (2010) 101602.
- [3] T. Hori, N. Fukuoka, T. Masuda, Y. Miyake, H. Yoshida, A. Fujii, Y. Shimizu, and M. Ozaki, submitted to *Sol. Energy Mater. Sol. Cells*
- [4] T. Hori, T. Masuda, N. Fukuoka, T. Hayashi, Y. Miyake, T. Kamikado, H. Yoshida, A. Fujii, Y. Shimizu, and M. Ozaki, submitted to *Adv. Mater.*

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