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

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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 photosorption 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 cm²/Vs and 0.5 cm²/Vs, respectively, in the crystalline phase of mesogenic non-peripheral octa(hexylphthalocyanine (C6PhC2), shown in Fig. 1[1]. C6PhC2 exhibits high absorption in the wavelength range of 500–850 nm corresponding to the Q-band, and C6PhC2 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 C6PhC2 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 C6PhC2 and discuss their photovoltaic properties by taking the microphase separation and photoinduced charge separation into consideration.

(PEDOT:PSS) was spin-coated onto an indium-tin-oxide (ITO)-coated quartz substrate, and dried in an oven under atmospheric conditions. P3HT, C6PhC2, PCBM were dissolved in chloroform. The P3HT:C6PhC2: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:C6PhC2:PCBM active layers, the composition ratios of which were 1:1 and 10:3:10, respectively. In the solar cell without C6PhC2, 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 C6PhC2, a high EQE of 46% at 730 nm originating from the absorption of C6PhC2 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.

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, C6PhC2, PCBM were dissolved in chloroform. The P3HT:C6PhC2:PCBM mixed solution was spin-coated onto the PEDOT:PSS layer in a glove box filled with argon gas.

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Figure 3 shows typical current-voltage characteristics of the solar cells with active layers of P3HT:PCBM and P3HT:C6PcH$_2$:PCBM, the composition ratios of which were 1:1 and 10:3:10, respectively, under AM1.5G (100 mW/cm$^2$) 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 C6PcH$_2$. The long-wavelength sensitivity in the EQE spectrum, as shown in Fig. 2, was improved by doping C6PcH$_2$, resulting in the enhancement of $I_{sc}$. The energy conversion efficiency of the solar cell without C6PcH$_2$ was 2.3% with $V_{oc}$ of 0.56 V, $I_{sc}$ of 8.6 mA/cm$^2$, and FF of 0.48, and that of the solar cell containing C6PcH$_2$ was improved to 3.0% with $V_{oc}$ of 0.56 V, $I_{sc}$ of 12.1 mA/cm$^2$ 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:C6PcH$_2$: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 C6PcH$_2$ (18.0 Å). At the P3HT:C6PcH$_2$:PCBM, the diffraction of C6PcH$_2$ appeared, although the diffraction intensity of P3HT was maintained. Therefore, it is considered that both P3HT and C6PcH$_2$ aggregate to form mutual microphase separation and that highly ordered P3HT domains and hexagonal columnar structures of C6PcH$_2$ coexist in the P3HT:C6PcH$_2$: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 C6PcH$_2$, 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:C6PcH$_2$: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/cm$^2$. 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 C6PcH$_2$ at the P3HT:C6PcH$_2$ composition ratio of 10:3 and that P3HT and C6PcH$_2$ 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:C6PcH$_2$:PCBM active layer.

References


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