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<td>Author(s)</td>
<td>Hori, Tetsuro; Miyake, Yasuo; Masuda, Tetsuya; Hayashi, Takeshi; Fukumura, Kaoru; Yoshida, Hiroyuki; Fujii, Akihiko; Ozaki, Masanori; Shimizu, Yo</td>
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Dependence of alkyl-substituent length for bulk heterojunction solar cells utilizing 1,4,8,11,15,18,22,25-octaalkylphthalocyanine

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Dependence of alkyl-substituent length for bulk heterojunction solar cells utilizing 1,4,8,11,15,18,22,25-octaalkylphthalocyanine

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Abstract. Bulk heterojunction organic thin-film solar cells utilizing soluble phthalocyanine derivatives, 1,4,8,11,15,18,22,25-octaalkylphthalocyanine (CnPcH2, n = 6, 7, 9, 10), were investigated. Two broad peaks existing in the external quantum efficiency spectra almost correspond to the Q-band and B-band of CnPcH2. The solar cell utilizing C6PcH2 had the best photovoltaic properties as evidenced by open-circuit voltage, short-circuit current density, fill factor, and energy conversion efficiency. Almost the same photovoltaic properties were observed in the solar cells utilizing C9PcH2 and C10PcH2. We discuss the photovoltaic properties by taking into consideration the crystal structure and electronic state of CnPcH2 from the results of the absorbance spectra, X-ray diffraction measurement, and polarization microscope observation. © 2012 Society of Photo-Optical Instrumentation Engineers (SPIE). [DOI: 10.1117/1.JPE.2.021004]

Keywords: organic thin-film solar cells; bulk heterojunction; phthalocyanine; solution process; 1,4,8,11,15,18,22,25-octaalkylphthalocyanine.

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1 Introduction

Organic thin-film solar cells utilizing organic semiconductors have attracted considerable attention as next-generation solar cells from the viewpoint of light weight, flexibility, and low cost. Such organic semiconductors are classified into two types: \( \pi \)-conjugated polymers and those having low molecular weight. Organic thin-film solar cells based on \( \pi \)-conjugated polymers have been investigated since the discovery of photoluminescence quenching, photoinduced charge transfer, and photoconduction enhancement in \( \pi \)-conjugated polymer-fullerene systems. Organic thin-film solar cells with a bulk heterojunction active layer fabricated by a wet process achieved high energy conversion efficiency. Wet processes are also important for the large area fabrication of organic thin-film solar cells.

On the other hand, some low-molecular-weight semiconductors demonstrate high crystallinity and charge mobility by intermolecular interactions; however, they are inappropriate for wet processes because of their poor solubility in typical organic solvents. Therefore, organic thin-film solar cells with a layered or p-i-n structure based on low-molecular-weight materials generally have been fabricated by thermal evaporation under vacuum. Recently, some groups have investigated solution-processable organic thin-film solar cells utilizing low-molecular-weight molecules, but device performance has still been low.
The control of intermolecular interactions is one of the most important strategies for the molecular design of organic semiconductors. The introduction of appropriate substituents is effective for the realization of a large area of uniform molecular packing for organic devices. Recently, we have demonstrated high hole and electron drift mobilities of 1.4 cm$^2$/Vs and 0.5 cm$^2$/Vs in the crystalline phase of a mesogenic phthalocyanine derivative, 1,4,8,11,15,18,22,25-octahexylyphthalocyanine (C6PcH$_2$, shown in Fig. 1), which was evaluated by means of time-of-flight (TOF) measurements. C6PcH$_2$ can be spread on a substrate from the solution and exhibits a mesogenic phase within a certain temperature range, which indicates that it can be used as a low-molecular-weight donor material for film fabrication by a solution process and for realizing high-performance bulk heterojunction organic solar cells.

C6PcH$_2$ could be mixed in a conventional solvent with a typical acceptor molecule, such as 1-(3-methoxy-carbonyl)-propyl-1-1-phenyl-(6,6)C$_{61}$ (PCBM), and the films fabricated by a solution process are available as a bulk heterojunction active layer in organic solar cells. Recently, we reported on a simple organic solar cell with bulk heterojunction of C6PcH$_2$ and PCBM fabricated by spin-coating, and demonstrated the high energy conversion efficiency of 3.1% and external quantum efficiency (EQE) higher than 70% at the Q-band region. Moreover, we reported on the active layer thickness dependence, hole transport buffer layer dependence, and tandem structure in an organic thin-film solar cell utilizing C6PcH$_2$. The properties of organic semiconductors, such as poly(3-alkylthiophene), strongly depend on the alkyl-substituent length. Therefore, alkyl-substituent length must be an important parameter for determining the electrical properties of CnPcH$_2$. Actually, C8PcH$_2$ exhibited different alignment and electrical properties than C6PcH$_2$. In this paper, we report on the alkyl-substituent length dependence of CnPcH$_2$ for simple bulk heterojunction organic solar cells.

2 Experimental Details

CnPcH$_2$ was synthesized according to the literature with slight modifications and fully purified by column chromatography (silica-gel with toluene as eluent) followed by repetitive recrystallization from toluene-methanol (1:2) solution. PCBM was purchased from Frontier Carbon Ltd.

The poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS, Baytron P VP AI 4083) was spin-coated onto an indium-tin-oxide (ITO)-coated quartz substrate at 1000 rpm for 60 s by using an aqueous solution diluted with the same volume of isopropanol and was dried at 100°C for 10 min in an oven under atmospheric conditions. The thickness of the PEDOT:PSS layer was estimated to be approximately 60 nm. The thickness was estimated by atomic force microscopy.

CnPcH$_2$ and PCBM were dissolved in chloroform solvent, and the composite ratio of CnPcH$_2$:PCBM was 2:1 by weight. The CnPcH$_2$:PCBM mixed solution was spin-coated onto the PEDOT:PSS layers at 500 rpm for 60 s in a glove box filled with argon gas. The thickness of the active layer was estimated to be approximately 150 nm.

An aluminum layer as a counter electrode to the ITO was deposited onto the composite layers through shadow masks by thermal evaporation under a pressure of approximately 10$^{-4}$ Pa. The evaporation speed and thickness of the Al layer were approximately 5 Å/s and 80 nm, respectively. The active area of the solar cell was 2 x 2 mm$^2$.

The absorbance spectra were measured using a spectrophotometer (Shimadzu UV-3150). X-ray diffraction (XRD) patterns were measured using a Rigaku X-ray diffractometer (RINT
The polarizing photomicrographs were measured by using a polarized optical microscope (Olympus BX50).

Carrier mobility was determined by the time-of-flight (TOF) technique. A N$_2$-pulsed laser (337 nm, 800 ps) was used to generate the photocarrier. The dc bias was applied by batteries. Transient photocurrents were detected by a digital oscilloscope (Hewlett Packard Infinium 54820A) with the help of a wide-band preamplifier. The mobility, $\mu$, was calculated by the equation $\mu = d^2/V\tau_s$, where $d$, $V$, and $\tau_s$ are sample distance, applied bias, and the transit time, respectively.

The photocurrent spectra were measured with a programmable electrometer (Keithley 617S) by using a xenon lamp light passing through a monochromator as a light source, and EQE was estimated for each incident light wavelength using the equation $\text{EQE}(\%) = \frac{1240 \times I(A/cm^2) \times 100}{\lambda(nm) \times P_{in}(W/cm^2)}$, where $I$ is the photocurrent density and $\lambda$ is the wavelength of incident light. The current-voltage characteristics were measured with a high-voltage-source measurement unit (Keithley 237) under AM1.5G (100 mW/cm$^2$) solar-illuminated conditions. From the current-voltage characteristics under AM1.5G, the FF and energy conversion efficiency ($\eta_e$) were estimated according to the following definitions: $\text{FF} = \frac{I_{max}V_{max}}{I_{sc}V_{oc}}$ and $\eta_e = \frac{I_{sc}V_{oc}FF}{P_{in}}$, where $I_{max}$ and $V_{max}$ are the current density and voltage at the maximum output power, respectively; $V_{oc}$ is the open-circuit voltage; $I_{sc}$ is the short-circuit current density; and $P_{in}$ is the intensity of the incident light. The current-voltage characteristics and EQE spectra were measured in a vacuum at room temperature.

## 3 Results and Discussion

Organic molecules such as porphyrins, phthalocyanines, and their derivatives exhibit anomalous optical characteristics because of their molecular ring structures. It is well known that they possess two kinds of energy bands, Q-band and B-band, in the case of phthalocyanines.$^{19}$

Figure 2(a) shows the absorption coefficient spectra of CnPcH$_2$ molecules in a chloroform solution. The concentration of solution is $1 \times 10^{-5}$ mol/L, and the optical path length is 1 cm. Figure 2(b) shows the absorbance spectra of CnPcH$_2$ thin films with thickness of 150 nm. The absorption coefficient spectra were independent of substituent length in a solution condition, and the absorption peak wavelengths of the Q-band were 700 and 730 nm. It is thought that the photoabsorption originates from the electronic transition of the ring $\pi$-conjugation on phthalocyanine and that the electronic energy states are independent of the substituent length in an isolated condition in the solution.

The absorbance spectra of thin films at the Q-band region differed between C6PcH$_2$ and the other CnPcH$_2$. The absorption peak wavelengths at the Q-band region of C6PcH$_2$ were 670 and 740 nm, and those of the other CnPcH$_2$ thin films were split around 640 and 770 nm. Moreover, the absorbance peak of C6PcH$_2$ was 0.75, and that of the other CnPcH$_2$ was about 0.5. It might be indicated that the different alignment of molecules in the C6PcH$_2$ film and the other CnPcH$_2$ films contribute to each electronic state.

![Absorption coefficient spectra of CnPcH$_2$ solution whose solvent is chloroform and (b) absorbance spectra of CnPcH$_2$ thin films, the thickness of which was 150 nm on quartz substrate.](image)

Fig. 2 (a) Absorption coefficient spectra of CnPcH$_2$ solution whose solvent is chloroform and (b) absorbance spectra of CnPcH$_2$ thin films, the thickness of which was 150 nm on quartz substrate.
Figure 3(a) shows the EQE spectra of the solar cells with a CnPcH2:PCBM active layer. Two broad peaks that almost correspond to the absorbance spectra in Fig. 2(b) are visible in the EQE spectra. The EQEs at both the 670 and 740 nm regions of the solar cell utilizing C6PcH2 were around 50% in spite of the different absorbance. Though the incident light of 740 nm was efficiently absorbed around the film surface, the generated charges could not reach the counter electrode.

The current-voltage characteristics of the solar cells utilizing CnPcH2 under the AM1.5G (100 mW/cm²) solar-illuminated condition are shown in Fig. 3(b). The highest photovoltaic properties in all parameters of $V_{oc}$, $I_{sc}$, FF, and $\eta_e$ were observed in the solar cell utilizing C6PcH2. The performance parameters of the solar cells utilizing CnPcH2 are summarized in Table 1. It is thought that the difference in $V_{oc}$ also suggests that the electronic states between C6PcH2 and the other CnPcH2’s are different.

Figure 4 shows the XRD patterns of the CnPcH2:PCBM bulk heterojunction films. In the XRD pattern of C6PcH2, a large diffraction peak corresponding to the distance of the hexagonal column was observed at around $2\theta = 4.86$ deg, and the second to the fourth harmonic diffraction peaks were also observed. It is thought that C6PcH2 formed hexagonal columnar structures with large domains in the bulk heterojunction film. On the other hand, in XRD patterns of the other CnPcH2’s, the diffraction intensities were weaker than those of C6PcH2, and two large diffraction peaks corresponding to the rectangular columnar structure appeared at around $2\theta = 4.27$ and 4.78 deg in C7PcH2, $2\theta = 3.96$ and 4.25 deg in C9PcH2, and $2\theta = 3.65$ and 4.49 deg in C10PcH2. Moreover, many small diffraction peaks were observed. These observations indicate that C6PcH2 has several domains with single hexagonal columnar alignment and that the other CnPcH2’s have many domains with various alignments mainly including the rectangular columnar alignment. In the rectangular structure, the column distance should be longer than the hexagonal structure, and the carriers are not transported easily between columns. As a result, the differences in the crystalline structure, such as the domain size of single alignment and the column distance, must be the main reason for the superiority of the electrical properties in C6PcH2:PCBM bulk heterojunction film.

Figure 5 shows polarizing photomicrographs of CnPcH2 at 25°C between ITO-coated glass substrates under cross-Nicol conditions. The cell gap between ITO-coated glass substrates is about 15 μm. In C6PcH2 many large crystal domains of more than 200 μm in length were observed. The high ambipolar carrier mobility, 1.08 cm²/Vs for hole and 0.5 cm²/Vs for

### Table 1

<table>
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<th>Material of active layer</th>
<th>$V_{oc}$ (V)</th>
<th>$I_{sc}$ (mA/cm²)</th>
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<th>$\eta_e$ (%)</th>
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<td>C6PcH2</td>
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<td>C7PcH2</td>
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<td>4.82</td>
<td>0.290</td>
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<td>C9PcH2</td>
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electron, was evaluated by the TOF technique. In the other CnPcH2’s, however, many small domains were observed, and carrier mobility could not be evaluated by the TOF technique, because of the dispersive decay curves of the transient. It is thought that the deep carrier trap at domain boundaries must be one reason for the dispersive decay curves of transient photocurrent observed in C7PcH2, C9PcH2, and C10PcH2. It is considered that the photovoltaic properties of the solar cell utilizing C6PcH2 are the highest because of the excellent electrical properties of large crystal domains with single hexagonal columnar structure alignment.

4 Conclusion

Bulk heterojunction organic thin-film solar cells utilizing the soluble phthalocyanine derivatives C6PcH2, C7PcH2, C9PcH2, and C10PcH2 were investigated. We found that the absorption
Coefficient spectra were independent of substituent length in a solution condition and that the electronic energy states are independent of substituent length in an isolated condition in the solution. The absorbance spectra of thin films at the Q-band region differed between C6PcH2 and the other CnPcH2's, however, and the different alignment of molecules in the C6PcH2 film as compared with the other CnPcH2 films contributes to each electronic state. Two broad peaks exist in the EQE spectra, which almost correspond to the Q-band and B-band of CnPcH2. The solar cell utilizing C6PcH2 has the highest photovoltaic properties in all parameters of Voc, Isc, FF, and ηe. Almost the same photovoltaic properties were observed in the solar cells utilizing C9PcH2 and C10PcH2. From the results of XRD measurement and polarization microscope observation, we found that C6PcH2 formed a hexagonal columnar structure and had many large crystal domains of more than 200 μm in length. On the other hand, other CnPcH2's formed a rectangular columnar structure and had many small domains with various alignments. The crystalline structure accounts for differences in the electrical properties of all CnPcH2's and makes C6PcH2∶PCBM bulk heterojunction film superior; therefore, the solar cell utilizing C6PcH2 displays the best photovoltaic properties.

Acknowledgments

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Biographies and photographs of the authors are not available.