Miscibility in Binary Blends of Non-Peripheral Alkylphthalocyanines and Their Application for Bulk-Heterojunction Solar Cells

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The fabrication of small-molecule bulk-heterojunction solar cells utilizing a mixed donor material composed of two types of soluble phthalocyanine derivatives with different substituent length has been studied. The power conversion efficiency (PCE) and short-circuit current density (J_{sc}) of the solar cells fabricated using the mixed donor material with an optimized mixture ratio reached 3.8% and 9.2 mA/cm², respectively, which were superior to those of organic solar cells utilizing each type of phthalocyanine derivative as a single donor material. The improvement of PCE and J_{sc} has been discussed from the viewpoints of the miscibility and carrier transport properties of the mixed donor material.

KEYWORDS

Organic Solar Cells; Bulk-Heterojunction; Phthalocyanine Derivatives; Mixed Donor Materials; Miscibility

1. Introduction

Since the discoveries of photoluminescence (PL) quenching, photoinduced charge transfer, and photoconduction enhancement between π -conjugated polymers and fullerenes [1-3], organic thin-film solar cells have attracted considerable attention as a promising alternative to inorganic solar cells from the variety of properties, such as mechanical flexibility, light-weight, potential for large-scale fabrication and utilization as a low-cost renewable energy source [4]. In particular, polymer bulk-heterojunction (BHJ) solar cells with a phase-separated active layer can be easily fabricated utilizing π -conjugated polymers as donor materials and fullerene derivatives as acceptor materials by a wet-process, and such solar cells have demonstrated a high power conversion efficiency (PCE) [5-7]. However, such polymers have the drawbacks of poor controllability of the molecular weight, difficulty in purification and low carrier mobility.

Solution-processed small-molecule bulk-heterojunction (SMBHJ) solar cells utilizing soluble small molecules as donor materials as well as conventional polymer BHJ solar cells have been considered to be among the most promising organic solar cell technologies in recent years [8-10].

In our previous works, SMBHJ solar cells utilizing the mesogenic phthalocyanine derivative 1,4,8,11,15,18,22,25-octaalkylphthalocyanine (C_nPcH_2) as a donor materials and fullerene derivatives as acceptor materials have been reported [11-14]. When $11 \leq n \leq 6$, C_nPcH_2 is a liquid crystalline organic semiconductor, and when $11 \leq n \leq 5$, C_nPcH_2 is soluble in common organic solvents. The compound, 1,4,8,11,15,18,22,25-octahexylphthalocyanine (C_6PcH_2) exhibits high hole and electron drift mobilities exceeding $1 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ and $0.5 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ in the crystalline phase, respectively [15]. Solar cells utilizing C_6PcH_2 and the fullerene derivative of 1-(3-methoxycarbonyl)-propyl-1-phenyl-(6,6)C₆₁ (PCBM) have demonstrated a PCE above 3% and an external quantum efficiency (EQE) higher than 70% in the Q-band region [11]. We also reported on the active layer thickness dependence, the hole transport

buffer layer dependence, the application to a tandem structure [12], alkyl substituent length dependence of CnPcH₂ [13, 14] and the doping effects of CnPcH₂ for polymer BHJ solar cells [16, 17]. We also attempted to control phase separation by utilizing processing additives in organic thin-film solar cells [18].

In order to improve the photovoltaic properties of solar cells, we focused on the miscibility of CnPcH₂ for analogue mixtures with different alkyl substituents. Miscibility is defined as the characteristic of mixing at the molecular level to produce one homogeneous mixture [19]. Mixed small-molecules with different alkyl substituents have miscibility unless the difference in alkyl substituent length between two components is too large [20].

Utilizing the concept of miscibility, improvement of the charge carrier mobilities has been reported. The hole mobility of binary mixture of triphenylene derivatives was obtained higher than the value of each material because of the increasing of charge-transfer integral [21]. In another study, each phthalocyanine derivative has different HOMO, LUMO level, nevertheless, the charge carrier mobilities of binary mixtures composed of the compounds was almost maintained that of each material [22]. On the other hand, molecular alignment control of mixed materials has been reported [23]. It is possible for the binary mixture composed of phthalocyanine derivatives with different alkyl substituents to continuously control the lattice parameter and the phase transition from Col_r phase to Col_h phase as a function of the mixture ratio. However, to our knowledge, organic electronic devices utilizing the mixtures controlled electronic properties have never been reported.

In this study, BHJ solar cells utilizing a mixture of 1,4,8,11,15,18,22,25-octapentylphthalocyanine (C5PcH₂) and C6PcH₂, the substituent lengths of which are different from each other, as a mixed donor material are studied. The photovoltaic properties of solar cells utilizing such mixtures are discussed by considering the miscibility, crystallinity and charge carrier mobility.

2. Experimental

The molecular structures of C5PcH₂, C6PcH₂ and PCBM and the device structure are shown in Fig. 1. C5PcH₂ and C6PcH₂ were synthesized in accordance with the literature [24] with slight modifications and fully purified by column chromatography (silica gel with toluene as an eluent) followed by repeated recrystallization from a toluene-methanol (1 : 2) solution. The PCBM was purchased from Frontier Carbon Ltd.

The solar cells were fabricated by the following process. 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 3000 rpm for 60 sec by using an aqueous solution diluted with the same volume of isopropanol. The substrate was then 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 30 nm.

C5PcH₂, C6PcH₂ and PCBM were dissolved in toluene. The molar ratio of the mixed donor material (comprising C5PcH₂ and C6PcH₂) to the acceptor material (PCBM) and the total molar concentration of the solutions were fixed to 2:1 and 15 mM, respectively. The C5PcH₂:C6PcH₂:PCBM mixed solution was spin-coated onto the PEDOT:PSS layer at 500 rpm for 60 sec in a glove box filled with nitrogen gas. The thickness of the active layer was estimated to be approximately 110-120 nm.

An aluminum (Al) layer, used as a counter electrode to the ITO, was deposited onto the composite layers through a shadow mask by thermal evaporation under a pressure of approximately 10⁻⁴ Pa. The thickness of the Al layer was approximately 80 nm. The active area of the solar cells was 2 × 2 mm².

The phase transition behavior of various mixtures of C5PcH₂:C6PcH₂:PCBM was investigated by differential scanning calorimetry (DSC, TA Instruments Q2000) and polarizing optical microscopy (POM, Nikon ECLIPSE E600 POL), where the microscope was equipped with a Mettler FP82HT hot stage and a Mettler FP90 central processor.

The absorbance spectra were recorded using a spectrophotometer (Shimadzu UV-3150). The highest occupied molecular orbital (HOMO) levels of C5PcH₂ and C6PcH₂ films were measured using a photoelectron spectrometer (Riken Keiki, AC-2). The film thickness was estimated by an atomic force microscope (AFM, KEYENCE VN-8000).

X-ray diffraction (XRD) patterns were measured using an X-ray diffractometer (Rigaku RINT 2000) with the Cu K α line. The d-spacing d was calculated from the XRD patterns using Bragg's law, $n\lambda = 2d\sin\theta$, and the crystallite size D was estimated from Scherrer's equation, $D = K\lambda/\beta\cos\theta$, where n is an integer, λ is the X-ray wavelength of 1.5418 Å, θ is the Bragg angle, K is the shape factor (0.9 was used in this study) and β is the full width at half-maximum. The lattice parameter a of C5PcH₂ and C6PcH₂ with the hexagonal lattice structure was calculated from the equation of $a = 2d(100)/\sqrt{3}$.

The carrier transport properties of mixtures were investigated by the time-of-flight (TOF) technique. A Nd:YAG pulsed laser (355 nm, 2 ns) was used as an excitation source, and the transient photocurrent was detected by a digital oscilloscope (LeCroy HDO 4054) with a wide-band preamplifier. The mobility μ was calculated by the equation $\mu = d^2 / V\tau_s$, where d is the film thickness, V is the applied bias and τ_s is the transit time.

The exciton diffusion length (L_D) of the mixed donor material was measured as a function of film thickness by PL quenching in bilayer structures of the C5PcH₂:C6PcH₂ mixture and C₆₀ [25, 26]. L_D was evaluated from the equation $Q(L) = (2L_D/L)\tanh(L/2L_D)$, where $Q(L)$ is the relative quenching efficiency as a function of film thickness L . Q was calculated from the equation; $Q = 1 - (\text{total PL of heterostructured sample} / \text{total PL of reference sample})$.

The photocurrent spectra and current density–voltage characteristics were measured in vacuum at room temperature with a source meter (Keithley 2400). The photocurrent spectra were measured using xenon lamp light passing through a monochromator as a light source, and the external quantum efficiency (EQE) was estimated for each incident light wavelength

using the equation $\text{EQE (\%)} = 1240 \times J \text{ (A/cm}^2\text{)} \times 100 / [\lambda \text{ (nm)} \times P_{\text{in}} \text{ (W/cm}^2\text{)}]$, where J is the photocurrent density, λ is the wavelength of incident light and P_{in} is the intensity of the incident light. The current density–voltage characteristics were measured under AM1.5G (100 mW/cm²) solar-illuminated condition, and FF and PCE were estimated according to the following the definitions; $\text{FF} = J_{\text{max}} V_{\text{max}} / J_{\text{sc}} V_{\text{oc}}$ and $\text{PCE} = (J_{\text{sc}} V_{\text{oc}} \text{FF} / P_{\text{in}}) \times 100$ where J_{max} and V_{max} are the current density and voltage at the maximum output power, respectively, J_{sc} is the short-circuit current density and V_{oc} is the open-circuit voltage.

3. Results and Discussion

Table I summarizes fundamental characteristics, such as the lattice parameter of the hexagonal columnar structures of C5PcH₂ and C6PcH₂, the hole mobility of C5PcH₂ and C6PcH₂, and the PCE of the C5PcH₂:PCBM and C6PcH₂:PCBM solar cells. C5PcH₂ is formed the smallest hexagonal lattice in the soluble C_nPcH₂, because of having the shortest alkyl substituent length among them. The difference of the lattice parameters between C5PcH₂ and C6PcH₂ is approximately 1.9 Å. The change of the lattice parameter must have strong relationship with the carrier transport and exciton dissociation processes in the active layer of organic solar cells. Therefore, if C5PcH₂ and C6PcH₂ have the miscibility, it is considered that the mixed donor materials could control the carrier transport properties by mixture ratio of them. In general, one of the important conditions of organic solar cells with high photovoltaic performance is that the active layers are formed by the materials with high charge carrier mobilities. The hole mobility of C5PcH₂ is relatively high in organic semiconductors, although it is an order of magnitude lower than that of C6PcH₂. In addition, since the organic solar cells utilizing C5PcH₂ and PCBM demonstrated high photovoltaic performance by optimization of donor-acceptor mixture ratio, C5PcH₂ should be a candidate material for mixing with C6PcH₂.

To confirm the miscibility of C5PcH₂ and C6PcH₂, the thermal properties in a mixture of C5PcH₂ and C6PcH₂ were investigated. The C5PcH₂ mixture ratio dependence of the DSC curves for C5PcH₂:C6PcH₂:PCBM mixtures is shown in Fig. 2(a). Two endothermic peaks corresponding to the melting and clearing points were observed in mixtures with 0 mol% to 50 mol% C5PcH₂. For C5PcH₂ mixture ratios of 75 mol% and 100 mol%, one endothermic peak at the melting point was observed. Moreover, for C5PcH₂ mixture ratios of 12.5 mol% and 25 mol%, the temperature difference between the clearing point and melting point was slightly greater than that for C6PcH₂, which seems to be relatively thermally stable

compared with the mixtures with other mixture ratios. The corresponding thermal behavior was also observed in POM images.

Figure 2(b) summarizes the phase transition diagram determined from the results of DSC and POM. The clearing points of the mixtures remained constant for mixtures with C5PcH₂ ratio lower than 50 mol%. The melting points coincided with Le Chatelier–Schröder relation [27-29], which theoretically describes the thermal behavior of the melting point for each mixture ratio. The eutectic point of the mixture was approximately determined to be at the C5PcH₂ mixture ratio of 23 mol% from the calculation using Le Chatelier–Schröder relation. Therefore, these results indicate that the mixtures have miscibility, and that each material is mixed at the molecular level.

Figure 3 shows POM images of the mixture composed of C5PcH₂ and C6PcH₂ with various C5PcH₂ mixture ratios. Samples were prepared by sandwiching the mixture between two glass substrates. In the range of mixture ratio with both crystal and LC phases, the similar texture to C6PcH₂ was obtained. On the other hand, in the range of mixture ratio with only crystal phase, the texture was almost similar to that of C5PcH₂. Thus, the textures depending on the phase transition diagram in Fig. 2(b) were observed.

Figure 4 shows the C5PcH₂ mixture ratio dependence of the current density–voltage characteristics of solar cells utilizing various mixtures under the AM1.5G (100 mW/cm²) solar-illuminated condition, and the photovoltaic properties are summarized in Table II. The V_{oc} of the solar cells remained constant regardless of the C5PcH₂ mixture ratio. This is because the HOMO levels of C5PcH₂ and C6PcH₂ are 5.24 eV and 5.22 eV, respectively. The FF of the solar cells was almost constant with C5PcH₂ mixture ratio below 50 mol%. Above C5PcH₂ mixture ratio of 50 mol%, FF, PCE and J_{sc} decreased with increasing C5PcH₂ mixture ratio.

The PCE and J_{sc} of the solar cell in the case of the C5PcH₂ mixture ratio of 25 mol% reached 3.8% and 9.2 mA/cm², respectively, which were higher than those of the

C5PcH₂:PCBM and C6PcH₂:PCBM solar cells. For C5PcH₂ mixture ratios above 25 mol%, PCE and J_{sc} tended to decrease with increasing C5PcH₂ mixture ratio.

The C5PcH₂ mixture ratio of 25 mol% is the closest to the eutectic point in the phase transition diagram. The improvement of the photovoltaic properties seems to be due to utilizing the one homogeneous mixture with two uniformly mixed donor materials. In the case of C5PcH₂ mixture ratio above 25 mol%, it is considered that the homogeneous mixture partly collapsed and that the formed domains of C5PcH₂ became dominant for the photovoltaic properties.

Figure 5 shows the C5PcH₂ mixture ratio dependence of the EQE spectra of the solar cells utilizing various mixtures of C5PcH₂ and C6PcH₂. The absorption peaks of C5PcH₂ and C6PcH₂ films are located at 300-400 nm and 600-800 nm, which originate from the B- and Q-bands of phthalocyanine, respectively [11]. Although the absorbance spectra of the mixed films of C5PcH₂ and C6PcH₂ are almost the same for all mixture ratios of C5PcH₂, as clearly shown in Fig. 6, the EQE of the solar cell with C5PcH₂ mixture ratio of 25 mol% was 10% higher than that of the C6PcH₂:PCBM solar cell at the Q-band. Since a marked difference in EQE spectrum was observed in spite of the similar absorbance spectra, the charge carrier transport properties should be mainly associated with the improved EQE.

Figure 7 shows the C5PcH₂ mixture ratio dependence of the charge carrier mobilities in the mixtures of C5PcH₂ and C6PcH₂. In the case of C5PcH₂ mixture ratio below 25 mol%, the hole mobility decreased with increasing C5PcH₂ mixture ratio, and the electron mobility remained constant. As a result, the difference between the hole and electron mobilities became small at the C5PcH₂ mixture ratio of 25 mol%. The balance of the hole and electron mobilities is considered to be effective for the improvement of J_{sc} , PCE and EQE. In contrast, the hole and electron mobilities of the mixtures were suppressed at C5PcH₂ mixture ratios above 25 mol%, which is considered to be strongly related to the decrease in J_{sc} .

Figure 8(a) shows XRD patterns of BHJ active layers comprising C5PcH₂:C6PcH₂:PCBM for each mixture ratio and Fig. 8(b) shows the C5PcH₂ mixture ratio dependence of the lattice parameter and crystallite size estimated from the XRD patterns using Bragg's law and Scherrer's equation, respectively. The diffraction peaks at approximately $2\theta=4.9^\circ$ and $2\theta=5.3^\circ$ correspond to the lattice parameter of the hexagonal columns formed by C6PcH₂ and C5PcH₂, respectively. As shown in Fig. 8(a), a single peak was observed around 5° from each mixture film, which could not be explained by the overlapping of the original peaks of C5PcH₂ and C6PcH₂. With increasing C5PcH₂ mixture ratio, the single peak continually shifted to a larger angle.

According to a previous report on mixed liquid crystals, when the difference between the lattice parameters of two materials is smaller than 15%, the mixture tends to have miscibility [30]. The difference between the lattice parameters of C5PcH₂ and C6PcH₂ satisfies the above condition, which also supports that the mixture of C5PcH₂ and C6PcH₂ possesses miscibility from the viewpoint of molecular alignment.

Moreover, the crystallite size of the mixtures continuously decreased with increasing C5PcH₂ mixture ratio. The crystallite size tends to be related to the exciton diffusion length L_D . Maximum J_{sc} and PCE are obtained when L_D is approximately equal to the crystallite size [31, 32]. The L_D in the C5PcH₂ film and in the mixture film of C5PcH₂ and C6PcH₂ with C5PcH₂ mixture ratio of 25 mol% were estimated to be approximately 35 nm and 36 nm, respectively, by the PL quenching method.

The L_D of the mixture film with C5PcH₂ mixture ratio of 25 mol% almost coincided with the crystallite size (35 nm). It is considered that the C5PcH₂:C6PcH₂:PCBM solar cell with the mixture ratio demonstrated the maximum J_{sc} and PCE because photogenerated excitons in C5PcH₂ and C6PcH₂ can be efficiently dissociated into free charge carriers in the donor/acceptor interface and recombination of the charge carriers is relatively suppressed. Control of the crystallite size via the mixture ratio of the mixed donor materials seems to be

an appropriate method for the obtaining high photovoltaic properties according to the results in this study.

4. Conclusions

SMBHJ solar cells utilizing a mixed donor material comprising C5PcH₂ and C6PcH₂ were demonstrated. When the mixture ratio in C5PcH₂ of the C5PcH₂:C6PcH₂:PCBM solar cells was 25 mol%, the PCE and J_{sc} of the solar cell reached 3.8% and 9.2 mA/cm², respectively, which were higher than those of the C5PcH₂:PCBM and C6PcH₂:PCBM solar cells. Miscibility possessing the eutectic point was confirmed for the mixed donor material of C5PcH₂ and C6PcH₂. The improvement of photovoltaic properties was discussed in terms of the carrier transport properties and molecular alignment control of the mixed donor material.

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Figure captions:

Fig. 1. Molecular structures of C5PcH₂, C6PcH₂, and PCBM and device structure.

Fig. 2. (a) DSC curves showing heat flow (heating rate: 5 °C/min) for C5PcH₂:C6PcH₂:PCBM mixtures with various mixture ratios of C5PcH₂, and (b) phase transition diagram for the mixtures of C5PcH₂:C6PcH₂:PCBM.

Fig. 3. POM images of C5PcH₂:C6PcH₂ mixture with various C5PcH₂ mixture ratios (x).
POM images were taken at 165°C.

Fig. 4. C5PcH₂ mixture ratio dependence of current density-voltage characteristics in ITO/PEDOT:PSS/C5PcH₂:C6PcH₂:PCBM/Al solar cells under the AM 1.5G (100 mW/cm²) solar-illuminated condition.

Fig. 5. C5PcH₂ mixture ratio dependence of EQE spectra of the solar cells.

Fig. 6. C5PcH₂ mixture ratio dependence of absorbance spectra of the C5PcH₂:C6PcH₂ mixture films.

Fig. 7. C5PcH₂ mixture ratio dependence of charge carrier mobilities in C5PcH₂:C6PcH₂ mixture films.

Fig. 8. (a) XRD patterns and (b) C5PcH₂ mixture ratio dependence of lattice parameter and crystallite size of the C5PcH₂:C6PcH₂:PCBM films.

Figure 1

Figure 2

(a)

(b)

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

(a)

(b)

Table I. Lattice parameter, and hole mobility of C5PcH₂ and C6PcH₂, and PCE of the bulk-heterojunction solar cells utilizing C5PcH₂ and C6PcH₂.

Materials	Lattice Parameter	Hole Mobility (25 °C)	PCE
C5PcH ₂	19.2 Å	0.12 cm ² /Vs	1.8 % (C5PcH ₂ :PCBM = 1 : 2)
C6PcH ₂	21.1 Å	1.08 cm ² /Vs	3.1 % (C6PcH ₂ :PCBM = 2 : 1)

Table II. Photovoltaic properties of the solar cells with various C5PcH₂ mixture ratio.

Mixture Ratio of C5PcH ₂ (mol%)	V_{oc} (V)	J_{sc} (mA/cm ²)	Fill Factor	PCE (%)
0	0.82	7.2	0.52	3.1
12.5	0.82	8.8	0.51	3.7
25	0.82	9.2	0.51	3.8
50	0.82	7.8	0.50	3.3
75	0.82	6.5	0.43	2.3
87.5	0.81	5.5	0.39	1.8
100	0.81	4.6	0.38	1.4