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Miscibility in binary blends of non-peripheral alkylphthalocyanines and their application for bulk-heterojunction solar cells



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ABSTRACT

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.

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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 dem-

onstrated 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_nPcH₂) as a donor materials and fullerene derivatives as acceptor materials have been reported [11–14]. When $11 \geq n \geq 6$, C_nPcH₂ is a liquid crystalline organic semiconductor, and when $11 \geq n \geq 5$, C_nPcH₂ is soluble in common organic solvents. The compound, 1,4,8,11,15,18,22,25-octahexylphthalocyanine (C₆PcH₂) exhibits high hole and electron drift mobilities exceeding 1 cm² V⁻¹ s⁻¹ and 0.5 cm² V⁻¹ s⁻¹ in the

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crystalline phase, respectively [15]. Solar cells utilizing C6PcH₂ 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 C_nPcH₂ [13,14] and the doping effects of C_nPcH₂ 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 C_nPcH₂ 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 Al 4083) was spin-coated onto an indium-tin-oxide (ITO)-coated quartz substrate

at 3000 rpm for 60 s 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 s 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

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