



Macroscopically aligned molecular stacking structures in mesogenic phthalocyanine derivative films fabricated by heated spin-coating method



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ABSTRACT

Spin-coated films of a mesogenic phthalocyanine derivative, 1,4,8,11,15,18,22,25-octahexylphthalocyanine (C6PcH₂), with macroscopic alignment of molecular stacking structure were obtained by processing in liquid-crystal phase of C6PcH₂. The column axis direction of the hexagonal columnar structure of C6PcH₂ was determined by microscopic observation and polarized optical absorption measurement and was uniform in the millimeter-scale area. Highly ordered molecular stacking structure in the film, which is similar to the single crystal, was clarified by measurement of molecular tilting angle with respect to the column axis. The origin of the macroscopic molecular alignment during film formation was investigated by taking the process-temperature-dependent properties of the films into consideration.

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1. Introduction

The use of organic semiconductors is expected to allow electronic devices, such as thin-film transistors, photovoltaic cells, and light-emitting diodes, to be made more flexible, lighter and cheaper than current inorganic semiconductor-based devices. Early investigations into the physics of organic semiconductors were focused primarily on vapor-grown crystals [1–3], but there has been significant interest in solution-processes utilizing soluble materials [4–6]. Solution-processes, such as spin-coating and drop-casting, are effective for reducing fabrication cost of the devices. However, the fabricated organic semiconductor films tend to be polycrystalline with a considerable amount of grain boundaries, which interrupts the carrier transport in the films [7]. Therefore, for achieving highly-ordered crystalline structure through the solution-processed films, meniscus-guided coating processes, such as zone-casting [8], blade-coating [9], and off-center spin-coating [10] were proposed. In addition, crystallizable solvents mixed into solutions were reported to be effective for achieving highly-aligned semiconducting polymer films [11].

Thin-film fabrication by heated spin-coating has also been proposed, and utilizes the properties of liquid-crystal (LC) phases that have been observed in many soluble organic semiconductors containing a rigid π -conjugated moiety and a flexible substituent [12]. This method has already been demonstrated to produce a uniform film and marked enhancement in the carrier mobility of thin-film transistors [13]; however, there does yet appear to be any detailed studies into the macroscopic alignment of molecules in such films.

In this manuscript, we report on the heated spin-coating films of mesogenic phthalocyanine, 1,4,8,11,15,18,22,25-octahexylphthalocyanine (C6PcH₂). The properties of similar non-peripherally substituted phthalocyanines have been studied [14,15] and the high carrier mobility of exceeding $1.4 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in C6PcH₂ was reported [16]. In addition, C6PcH₂ is available for photovoltaic cells, the power conversion efficiency of which was reported to be exceeding 4% [17]. In this study, the highly-ordered C6PcH₂ films were fabricated by heated spin-coating method and the process temperature dependences of the textures of the films were discussed by taking the phase sequence of C6PcH₂ into account. In order to clarify the molecular stacking structure in the films, the measurements of anisotropic optical absorption, X-ray diffraction and optic axis direction of the films were carried out.

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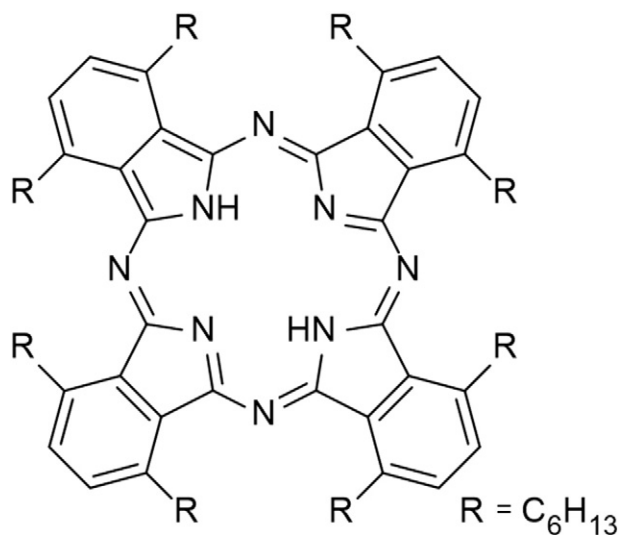


Fig. 1. Molecular structure of C6PcH₂.

2. Experimental details

Fig. 1 shows molecular structure of C6PcH₂. C6PcH₂ was synthesized and purified as reported previously [16], and dissolved with a concentration of 15 g L⁻¹ in 1,4-diethylbenzene, the boiling point of which is 184 °C, or chloroform for heated or non-heated spin-coating, respectively. The temperature of the spin-coating stage and the C6PcH₂ solution were controlled and kept during spin-coating process. In the spin-coating process, the cleaned glass substrate without any special modification was rotated at a speed of 500 rpm for 60 s under nitrogen atmosphere. Polarizing micrographs and optical absorption spectra of the films were taken by using a polarizing optical microscope (Nikon Eclipse LV100POL) and attached spectrometer (Hamamatsu PMA-11). The spot diameter of the light source for absorption measurement was approximately 100 μm. Out-of-plane X-ray diffraction patterns of the films were measured on a diffractometer (Rigaku SmartLab) using CuKα radiation ($\lambda = 0.15418$ nm). Optic axis directions in the films were measured by using the system consisting of two polarizers, a

photodiode and a semiconductor laser, the wavelength and the spot diameter of which were 532 nm and approximately 1 mm, respectively. Thicknesses of the films were obtained by measuring surface profiles at edges of the films, which were prepared by peeling a part of the film off, by an atomic force microscope (Keyence VN-8000) with contact mode. These observations of the samples were carried out at room temperature.

3. Results and discussion

3.1. Process-temperature-dependent domain size in the films

Fig. 2 shows the polarizing micrographs of the fabricated C6PcH₂ films, the thickness of which was 200–300 nm. The textures of the fabricated films changed depending on the process temperature as shown in Fig. 2(a) to (e). C6PcH₂ exhibits the LC phase between 161 and 170 °C upon heating, and between 140 and 170 °C upon cooling [16]. Therefore, the process temperatures for Fig. 2(a) and (b), Fig. 2(c) and (d), Fig. 2(e) are corresponding to the crystal phase, LC phase, and isotropic phase upon cooling, respectively.

At the process temperature corresponding to the crystal phase, although the domain size in the films gradually increased with increasing the process temperature, the optic axis directions of each domain were random, as shown in Fig. 2(a) and (b). In the film fabricated at room temperature then annealed at 150 °C for 10 min, the similar texture appeared as shown in Fig. 2(f). The heated spin-coating procedure in the crystal phase of C6PcH₂, that is, provided the similar effect with the post-annealing process at 150 °C.

In the case of the process temperature corresponding to the LC phase, in contrast to the films fabricated in the crystal phase, the optic axis directions of the domains seem to be almost uniform as be obvious in Fig. 2(c) and (d). In the micrographs with lower-power objective lens in Fig. 2(g) and (h), the optic axis in the film were uniaxially aligned in the large area with diameters of exceeding 1 mm, that is, the macroscopic molecular alignment appeared during film formation by spin-coating.

At the process temperature corresponding to the isotropic phase, the domain size of the films was suppressed markedly, and the optic axis directions of each domain were random. The uniform films could not be fabricated at the higher process temperature than 170 °C. In the case

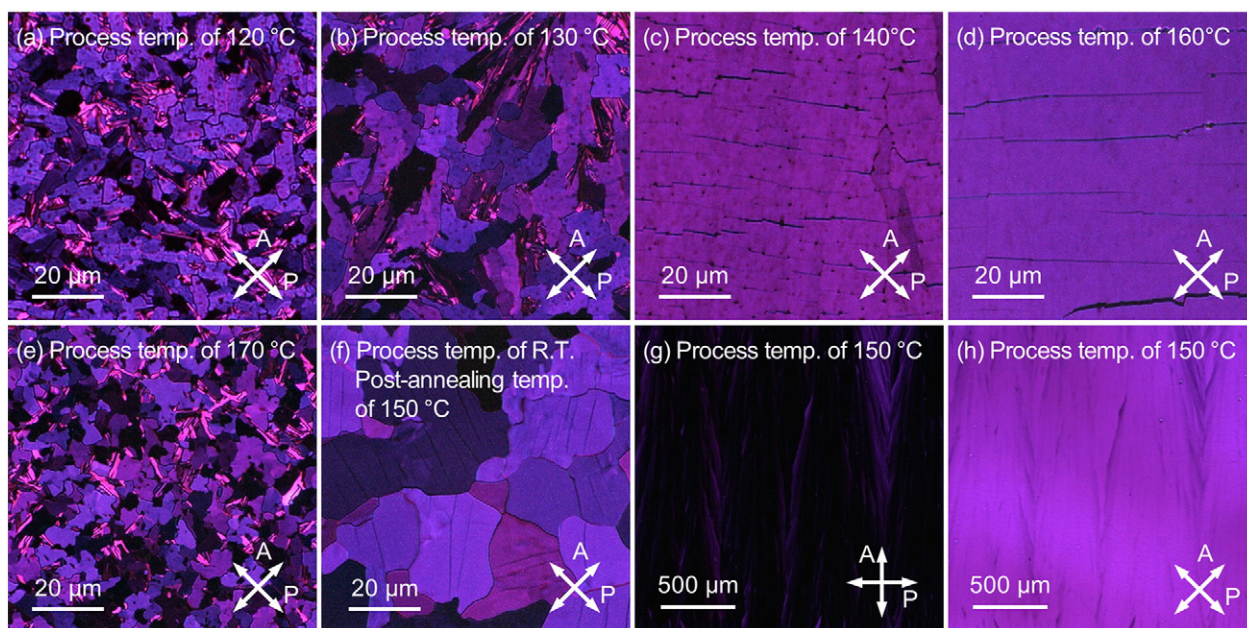


Fig. 2. Polarizing micrographs of the fabricated C6PcH₂ films. (a to e) The films fabricated at the process temperatures of between 120 and 170 °C. (f) The film fabricated at room temperature and annealed at 150 °C. (g, h) The film fabricated with the process temperature of 150 °C. The polarizers were rotated and a lower-power objective lens was used.

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