



Selective crystal growth in bar-coating process of polymorphic pentyl-substituted phthalocyanine thin film



Mitsuhiro Nakatani^a, Masashi Ohmori^a, Shusaku Nagano^b, Akihiko Fujii^{a,*}, Masanori Ozaki^a

^a Division of Electrical, Electronic and Information Engineering, Graduate School of Engineering, Osaka University, Suita, Osaka, 565-0871, Japan

^b Nagoya University Venture Business Laboratory, Nagoya, Aichi, 464-8603, Japan

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ABSTRACT

Molecularly oriented thin films of non-peripherally pentyl-substituted phthalocyanine (C5PcH₂), which exhibits α -type and β -type crystal polymorphs, were fabricated by the bar-coating method. By setting an α -type or β -type seed crystal around the initial position of the coating bar on a substrate, oriented thin films with either an α -type or β -type crystal structure were selectively fabricated, respectively. This was confirmed by grazing-incidence wide-angle X-ray scattering studies of the thin films. Without the seed crystal in the same bar-coating condition, an unidentified crystal polymorph of C5PcH₂ appeared in the film state, which was discussed by taking the peak intensities in the X-ray diffraction pattern into consideration.

1. Introduction

Phthalocyanines are disk-shaped and low-molecular-weight semiconductor materials with a π -conjugated system. Some of them form columnar structures, in which the molecules are stacked one-dimensionally, and exhibit high electrical conduction along their column axis [1]. Since the phthalocyanines also exhibit strong absorption in the visible region, electronic device applications, such as an organic solar cell (OSC) and organic field-effect transistor, have been proposed [2–4].

To realize the practical use of organic thin-film devices, printing methods, which enable large-area and mass production, have been studied in recent years [5–7]. Although conventional phthalocyanines are not suitable for thin-film fabrication by printing methods owing to their low solubility in typical organic solvents, the introduction of long-chain substituents enables the phthalocyanines to dissolve owing to the weakened intermolecular interaction [8]. In particular, an alkylphthalocyanine, the alkyl-substituents of which are introduced at non-peripheral positions, exhibits high solubility in an organic solvent and a uniform thin film can be easily fabricated by a typical solution process, such as spin-coating [9]. For example, the non-peripherally pentyl-substituted phthalocyanine 1,4,8,11,15,18,22,25-octapentylphthalocyanine (C5PcH₂), the molecular structure of which is shown in Fig. 1(a), was used as a donor material in a solution-processed OSC with a bulk heterojunction, and a high conversion efficiency of 3.5% was demonstrated [10]. In addition, C5PcH₂ exhibits high ambipolar carrier mobilities of 0.19 cm²V⁻¹s⁻¹ for holes and 0.05 cm²V⁻¹s⁻¹ for

electrons according to time-of-flight measurement [11]. Such excellent electrical properties should originate from the molecular packing structure of C5PcH₂ in the solid state.

C5PcH₂ exhibits two crystal polymorphs, α -type and β -type crystals [12,13], the molecular packing structures of which are shown in Fig. 1(b) and (c), respectively. The α -type crystal of C5PcH₂ irreversibly transfers to the β -type crystal upon heating [12]. The α -type crystal of C5PcH₂ is based on the triclinic structure, in which all molecules are tilted in the same direction and the lattice parameters are $a = 5.14406(13)$ Å, $b = 16.7097(4)$ Å, $c = 18.6864(13)$ Å, $\alpha = 92.730(7)^\circ$, $\beta = 94.415(7)^\circ$, and $\gamma = 91.667(7)^\circ$. In contrast, the β -type crystal is based on the monoclinic structure, in which molecules are alternately tilted and the lattice parameters are $a = 19.3788(5)$ Å, $b = 9.7975(3)$ Å, $c = 34.289(2)$ Å, $\alpha = 90^\circ$, $\beta = 91.781(7)^\circ$, and $\gamma = 90^\circ$.

The α -type crystal of C5PcH₂ tends to grow slowly, while the β -type crystal is obtained with a relatively fast growth rate. In a solution process for obtaining a thin film of C5PcH₂, such as spin-coating, only the β -type polycrystal exists in the film during the rapid film formation [10,11,14], and α -type crystal formation in a C5PcH₂ thin film has not been reported. According to a theoretical prediction of the carrier transport using density functional theory, the hole mobilities in the α -type and β -type C5PcH₂ crystals were estimated to be 7.51 and 0.30 cm²V⁻¹s⁻¹, respectively, that is, the hole mobility in the α -type crystal should be about 25 times higher than that in the β -type crystal [15]. Therefore, a preparation technique to obtain a thin film of the α -type

* Corresponding author.

E-mail address: afujii@eei.eng.osaka-u.ac.jp (A. Fujii).

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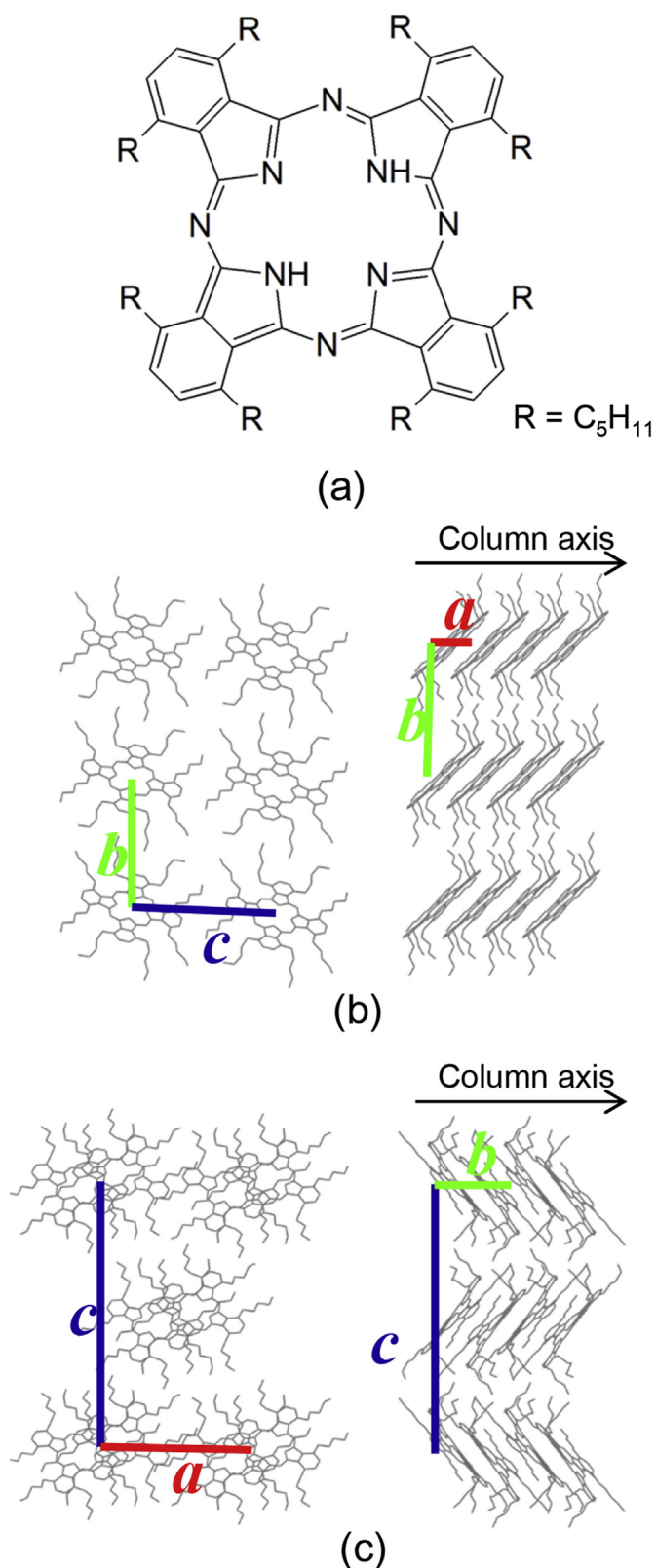


Fig. 1. Molecular structure of C5PcH₂ (a) and molecular packing structures of α -type (b) and β -type (c) of C5PcH₂, which are viewed in the direction parallel and perpendicular to the column axis. In the molecular packing structure, the red, green, and blue lines indicate *a*, *b*, and *c* axes, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

C5PcH₂ crystal is desirable for realizing high-performance electronic devices.

Recently, a bar-coating method has been reported as a solution process for fabricating a molecularly oriented thin film involving the crystal growth of a homologue molecule of C5PcH₂, 1,4,8,11,15,18,22,25-octahexylphthalocyanine (C6PcH₂). In the bar-coating method, the unidirectional motion of a coating bar, the speed of which can be controlled to be comparable to the crystal growth rate, enables a uniaxial molecular orientation as well as large-area film formation [16,17]. The bar-coating method has not yet been adopted for other alkyl-substituted phthalocyanines including C5PcH₂. By controlling the coating conditions, such as the sweep speed of the coating bar, the substrate temperature, the solution concentration, and the solvent species, it might be possible to selectively generate each crystal polymorph of C5PcH₂ in molecular oriented thin films.

In this study, a seed crystal was set around the initial position of the coating bar on a substrate in thin-film fabrication by the bar-coating method to realize molecularly oriented thin films of C5PcH₂. The crystal structure in the thin films was investigated by grazing-incidence wide-angle X-ray scattering (GIWAXS), and the molecular packing structure and molecular orientation were discussed.

2. Experimental methods

C5PcH₂ was synthesized in accordance with the literature [18] 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 [19]. Needle-like microcrystals obtained by the recrystallization were used as an α -type seed crystal, the crystal type of which was confirmed by the powder X-ray diffraction (XRD). For preparing β -type seed crystals, the thermal phase transition from the α -type to β -type crystal [12] was used; small pieces of the α -type crystals were heated at 230 °C for 1 h to induce the phase transition to the β -type crystals.

A thin film of C5PcH₂ was fabricated in the following process. A glass substrate was cleaned with a cleaning agent (Furuuchi Chemical Semico Clean 56) and distilled water by ultrasonication, then treated with UV-ozone. The substrate was placed on a hotplate and the substrate temperature was set at 40 °C. A powder of the α -type or β -type seed crystal was put onto the substrate, and a 9.6-mm-diameter coating bar wound with a 0.05-mm-diameter metal wire was set onto the substrate. The seed crystals were located around the initial position of the coating bar. A chloroform solution of C5PcH₂, the concentration of which was 20 g/L, was dropped onto the coating bar, then the coating bar was moved in the horizontal direction at a constant sweep speed of 200 μ m/s. Confirming the seed crystal effect on the crystal growth, the bar coating without any seed crystals was also carried out. The schematic diagram of the bar-coating method is shown in Fig. 2.

The thin film was observed by a polarized optical microscope (POM) (Nikon Eclipse LV 100 POL) under crossed nicols. The surface morphology and thickness of the thin films were observed by an atomic force microscope (AFM) (Shimadzu SPM-9700).

The crystal structure and molecular orientation in the thin film were determined by a GIXAXS measurement system using a Rigaku FR-E X-ray diffractometer with a Rigaku R-AXIS IV 2D detector. The schematic

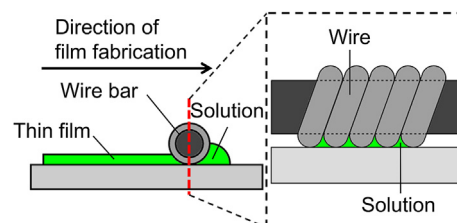


Fig. 2. Schematic diagram of the bar-coating method.

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