Organic Electronics 60 (2018) 16–21

Contents lists available at ScienceDirect

Organic Electronics

journal homepage: www.elsevier.com/locate/orgel

Single-crystalline thin-film growth via solution-mediated polymorphic transformation of octahexyl-substituted phthalocyanine and its optical anisotropy

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ABSTRACT

The fabrication of a single-crystalline thin film of non-peripheral octahexyl-phthalocyanine ($C6PcH_2$) was realized by performing a tetrahydrofuran (THF) vapor treatment on a the spin-coated film. The solution-mediated polymorphic transformation of $C6PcH_2$ was promoted in the THF vapor, and a single-crystalline thin film with α-phase crystal grew in the thin film when setting an appropriate temperature. The thin film exhibited optical anisotropy, such as a high dichroic ratio, and the color of the transmitted light varied from green to transparent depending on the polarization direction. The molecular packing structure on the substrate was determined by X-ray diffraction and polarized absorption measurements.

1. Introduction

Organic semiconductors have attracted considerable attention for device applications, because of their flexibility and light weight compared with inorganic semiconductors [1,2]. Moreover, some organic materials possessing high solubility in typical solvents have high potential to reduce the production cost of electronic devices. Among the organic semiconducting materials, phthalocyanine, which is a well-known organic semiconductor, exhibits thermal and chemical stability and excellent electrical properties. Although the solubility of non-substituted phthalocyanine in organic solvents is extremely low [3–6], the non-peripherally alkyl-substituted phthalocyanines developed by Cook et al., exhibit liquid crystalline properties as well as high solubility in organic solvents [7–9]. Liquid-crystalline properties are also attractive for the self-organization of highly ordered molecular packing structures and high carrier mobility in thin-film devices, such as field-effect transistors [10,11].

A non-peripherally alkyl-substituted phthalocyanine 1,4,8,11,15,18,22,25-octahexylphthalocyanine ($C6PcH_2$) has been reported to exhibit high ambipolar carrier mobilities of 1.4 and 0.5 $cm^2 V^{-1} s^{-1}$ for holes and electrons, respectively, in the crystal phase, estimated by the time-of-flight technique [12]. The molecular structure is shown in Fig. 1(a). To understand the reason for such high mobility, a simulation based on density functional theory was carried out by taking the single-crystal structure of $C6PcH_2$ into account [13]. In our previous analysis of the single-crystal analysis of $C6PcH_2$ [14], two crystal polymorphs were found, which are called the α-phase and β-phase crystals and are based on triclinic and monoclinic lattices, respectively, as shown in Fig. 1(b) and (c). According to a theoretical prediction, the hole mobilities in the α-phase and β-phase are 11.63 and 1.486 $cm^2 V^{-1} s^{-1}$, respectively, that is, the α-phase crystal shows a mobility 10 times higher than the β-phase [13]. The optical and electrical properties of thin films based on the β-phase have been extensively investigated [15–18], because the β-phase crystal tends to preferentially appear in the thin-film fabrication. Recently, it was reported that the crystal structure in thin film changes from β-phase to α-phase upon performing solvent vapor treatment, which promotes a solution-mediated polymorphic transformation, resulting in α-phase single-crystalline thin-film growth [19]. However, the detailed conditions required for α-phase crystal growth and the optical properties of the α-phase single-crystalline thin film were not clarified.

In this study, α-phase single-crystalline thin films of $C6PcH_2$ were fabricated by solvent vapor treatment at various temperatures, and the appropriate growth conditions are discussed by taking the Gibbs free energy of the polymorphs into consideration. To clarify the molecular packing structure in the thin films, X-ray diffraction and polarized absorption measurements were carried out.

2. Experimental section

$C6PcH_2$ was synthesized by the chemical procedure reported previously [20]. $C6PcH_2$ was dissolved in chloroform at a concentration of

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https://doi.org/10.1016/j.orgel.2018.05.029
Received 5 February 2018; Received in revised form 27 April 2018; Accepted 20 May 2018

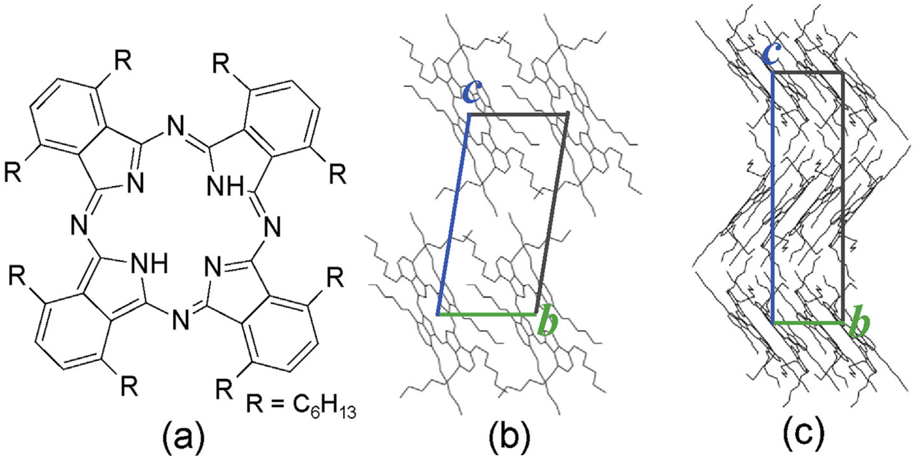

Fig. 1. Molecular structure of C6PcH$_2$ (a), and the crystal structures of α-phase (b) and β-phase (c).

60 g L^{-1} and the solution was spin-coated onto a precleaned glass or Si substrate at a speed of 1000 rpm for 60 s. The thickness of the C6PcH$_2$ film, which was estimated by atomic force microscopy (Keyence VN-8000), was approximately 500 nm. To promote the solution-mediated polymorphic transformation, the spin-coated C6PcH$_2$ thin film was exposed to tetrahydrofuran (THF) vapor in a closed vessel at 10, 20, 30, or 40 °C for two days. In our previous report, *p*-xylene was used in the solvent vapor treatment of a C6PcH$_2$ thin film [19]. After testing various solvents as a vapor solvent, THF was adopted as the solvent in this study because of its relatively high vapor pressure and the stable solution-mediated polymorphic transformation from β-phase to α-phase crystal.

The thin films were observed by a polarized optical microscope (POM) (Nikon Eclipse LV 100POL). An out-of-plane θ-2θ scan of the X-ray diffraction (XRD) of the thin films was carried out using an X-ray diffractometer (Rigaku SmartLab) with CuKα radiation ($\lambda = 0.15418$ nm).

The optical absorption spectrum of the thin film was measured using a spectrophotometer (Shimadzu UV-3150). The polarized absorption spectrum of the thin films was measured using a spectrometer (Hamamatsu PMA-11) attached to the microscope. The spot diameter of the light source was 100 μm.

3. Results and discussion

Fig. 2 shows the reflection images of the C6PcH$_2$ thin films on Si substrates, which were observed by the POM with crossed polarizers. POM images of the C6PcH$_2$ thin films treated by the THF vapor at 10, 20, 30, and 40 °C, are shown in Fig. 2(a)–(d), respectively. Before the THF vapor treatment, a dark image was obtained, corresponding to the deposited spin-coated film, while dark blue domains appeared after the THF vapor treatment at 10–30 °C as shown in Fig. 2(a)–(c). The domain size depended on the process temperature, and the typical domain width and length at 30 °C reached sub-millimeter and millimeter orders, respectively. The generation of such large domains can be explained by the solution-mediated polymorphic transformation as reported previously [19]. Carrying out the THF vapor treatment at 40 °C, a completely different texture, which was composed of small domains, was obtained as shown in Fig. 2(d).

Fig. 2(e) and (f) show typical POM images of the monodomain crystal during the growth at 30 °C in the extinction and diagonal positions, respectively. In the extinction position of the crossed polarizers, the rectangular and large monodomain did not become completely dark; therefore, the monodomain appeared to be a biaxial single crystal.

XRD patterns of the spin-coated films without and with the THF vapor treatment at 30 and 40 °C are shown in Fig. 3. In the spin-coated thin film of C6PcH$_2$, a peak at $2\theta = 4.81°$, which corresponds to the (0 0 2) plane of the β-phase crystal [14], was observed. In the XRD pattern of the thin film after the THF vapor treatment at 30 °C, a peak at $2\theta = 4.49°$, which corresponds to the (0 0 1) plane of the α-phase crystal [14], appeared. In the case of the THF vapor treatment at 40 °C, a peak was confirmed at $2\theta = 4.90°$, which is also based on the (0 0 2) plane of the β-phase crystal. Therefore, the solution-mediated polymorphic transformation from the β-phase to α-phase occurred upon performing the THF vapor treatment at 10–30 °C in this study, and the (0 0 1) plane of the α-phase crystal tended to be parallel to the substrate surface. Altough a different texture was observed after the THF vapor treatment at 40 °C, the crystal structure in the thin film still corresponded to the β-phase.

To clarify the thermal stability of the polymorphs, the difference in the Gibbs free energies between the polymorphs was investigated. The differences of the Gibbs free energy, enthalpy, and entropy between the α-phase and β-phase, which are expressed as ΔG, ΔH, and ΔS, were calculated by using [21].

$$\Delta G = \Delta H - T\Delta S\ , \tag{2}$$

$$\Delta H = \int_{T}^{T_t} (C_\alpha - C_\beta)dT + \Delta H_t, \tag{3}$$

$$\Delta S = \int_{T}^{T_t} \left(\frac{C_\alpha}{T} - \frac{C_\beta}{T}\right)dT + \frac{\Delta H_t}{T_t}, \tag{4}$$

where C_α and C_β are the heat capacities of the α-phase and β-phase, respectively, and depend on the temperature. T_t is the solid state transition temperature from the α-phase to β-phase and ΔH_t is the transition enthalpy from the α-phase to β-phase. The C_α, C_β, T_t, and ΔH_t were evaluated by using the result of a previous differential scanning calorimetry (DSC) measurement of C6PcH$_2$ [22]. In particular, T_t and ΔH_t were determined to be 354 K and 41.2 kJ/mol, respectively. Then, ΔG, ΔH, and ΔS at 30 °C were calculated to be 4.38 kJ/mol, 24.8 kJ/mol, and 6.75×10^{-2} kJ/molK, respectively. The Gibbs free energy of the α-phase is lower than that of the β-phase at 30 °C, thus explaining why the solution-mediated polymorphic transformation from the β-phase to α-phase took place at 30 °C. ΔG decreases with increasing temperature, becoming 3.60 kJ/mol at 40 °C. It is considered, therefore, that the temperature setting at 40 °C inhibited the solution-mediated