Macroscopically Aligned Molecular Stacking Structures in Mesogenic Phthalocyanine
Derivative Films Fabricated by Heated Spin-coating Method

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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.

Keywords

Spin-coating; Thin film; Fabrication; Liquid-crystal; Phthalocyanine; Molecular alignment; Anisotropic absorption; Solution process

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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 cm²V⁻¹s⁻¹ in C6PcH₂ were 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.

2. Experimental details

Figure 1 shows molecular structure of C6PcH₂. C6PcH₂ was synthesized and

purified as reported previously[16], and dissolved with a concentration of 15 gL^{-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 seconds 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 $100 \text{ }\mu\text{m}$. Out-of-plane X-ray diffraction patterns of the films were measured on a diffractometer (Rigaku SmartLab) using CuK α radiation ($\lambda = 0.15418 \text{ nm}$). 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

Figure 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 Figs. 2(a) to 2(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 Figs. 2(a) and 2(b), Figs. 2(c) and 2(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 Figs. 2(a) and 2(b). In the film fabricated at room temperature then annealed at 150 °C for 10 minutes, 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 Figs. 2(c) and 2(d). In the micrographs with lower-power objective lens in Figs. 2(g) and 2(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 of the process temperature of 170 °C, the smooth film could be obtained, which might be explained by the decrease of the substrate temperature into the range of the LC phase due to the sample stage rotation and solvent evaporation during spin-coating process. After the film formation, the substrate temperature returned to the range of isotropic phase, therefore, the optic axis direction of domains might be disarranged.

Although several solution-based fabrication methods for organic semiconductor films with large-area molecular alignment have been reported[9,11,18], the fabrication by conventional spin-coating has not been reported. Since the highly ordered C6PcH₂ films were obtained when the process temperature was in the LC phase, it is considered

that the macroscopic flow of molecules in LC phase during fabrication must affect the molecular alignment in the film. In some of the films, actually, macroscopic directions of optic axes tended to be rotationally symmetric around a rotation axis of a spin-coating stage. Since the flow-assisted molecular alignments in the LC phase materials seem to be critical for this method, further investigations on the effects with taking thermotropic and lyotropic LC phases into consideration are needed.

3.2. Process-temperature-dependent crystallinity of the films

For clarifying the crystallinity and the direction of the column axis of the C6PcH₂ film fabricated by heated spin-coating method, X-ray diffraction patterns were measured. As shown in Fig. 3(a), the strong diffraction peaks were observed at $2\theta = 4.9^\circ$, which originate from the inter-column distance of the hexagonal columnar structure according to previous reports on the crystalline structure of C6PcH₂ single crystal[19,20]. The diffraction peak intensity depended on the process temperature, and the peaks with the higher-order diffraction were obviously observed when the process temperature was 150 °C. As shown in Fig. 3(b), the full-width half-maximum (FWHM) for the first order diffraction peaks decreased depending on the process temperature. The slight shift of the peak angle, which is considered to result from considerable distribution of inter-column distance in low-ordered films, were also observed.

Therefore, the film formation in the LC phase is effective for achieving enhanced crystallinity.

Additionally, the distribution of the column axis direction in the film with respect to the substrate was measured. Direction of the diffraction vector was fixed and the diffraction angle θ was set for the first-order diffraction peak. Then the normal vector of the sample was tilted by an angle χ with respect to the fixed diffraction vector of the measurement system. As shown in Fig. 3(c), the maximum intensity was observed at $\chi = 0^\circ$ in each fabricating condition, which indicates the planar alignment of the C6PcH₂ column with respect to the substrate, and the minimum FWHM for the distribution was also obtained when the process temperature was 150 °C.

3.3. Molecular orientations in the π -stacked columns

From the results of the textures and X-ray diffraction of the films fabricated at the process temperatures corresponding to the LC phase, the anisotropic optical properties based on the planarly aligned columns of C6PcH₂ were prospective. Since the temperature dependence of the crystalline structure of C6PcH₂ was reported[20], it is considered that long crack lines observed in Figs. 2(c) and 2(d) appear upon cooling and direction of crack line have a strong relationship with that of column axis. Figure 4 shows the polarized absorption spectra of the C6PcH₂ films fabricated at the process

temperature of 150 °C. The absorbance based on the Q-band of phthalocyanine became maximum and minimum when the polarizing direction of the incident light was parallel and perpendicular to the crack direction, respectively. Since the transition dipole moments correspond to the optical absorption for the Q-band are in plane of the phthalocyanine molecules, it is considered that azimuth directions of normal vectors of the C6PcH₂ molecules oriented perpendicular to the crack direction. It is considered, therefore, that the column axis in the film was oriented to be perpendicular to the crack direction in the plane of the film.

In order to determine the tilting angle of C6PcH₂ molecules with respect to the column axis, the optic axis direction in the films was measured by using the system shown schematically in Fig. 5(a). The C6PcH₂ film fabricated with the process temperature of 150 °C was fixed on a sample holder with a rotation axis between two crossed polarizers, and the transmitted light was detected with rotating the film as shown in Fig. 5(a). The direction of the column axis in the film was confirmed in advance by measuring anisotropic absorption spectra as described above and set perpendicular to both of the incident light and the rotating axis. In addition to the measurement, the dependence of transmitted light intensity on the tilting angle of the molecules was also calculated. The calculation was based on the presumptions that the

column axis direction was distributed as obtained by X-ray diffraction measurement, that the part of the incident light was reflected based on Fresnel reflection, and that the average refractive index of the film was 1.5.

As shown in Fig. 5(b), the intensity of the transmitted light depended on the rotating angle and the intensity became minimum when the rotating angle was approximately -40° , which indicates that the direction of optic axis of the C6PcH₂ molecules denoted as n_e in Fig. 5(a) was parallel to the incident light. Since the measured results coincided with the calculated data with the assumed optic axis direction tilting by 24° with respect to incident light, it is considered that the normal vectors of the C6PcH₂ molecules were tilted by 66° with respect to the column axis direction. The obtained tilting angle is in agreement with previously reported value of 64° , which was focused on the single crystals of C6PcH₂[19,20]. Therefore, although it is the non-equilibrium fabrication method, highly ordered crystalline structure was obtained by simply controlling the process temperature.

4. Conclusions

In summary, we fabricated the highly ordered C6PcH₂ films by the heated spin-coating method. The column axis direction of the hexagonal columnar structure of C6PcH₂ was uniform in the large area with the diameters of exceeding 1 mm. The

relationship between the flow in the LC state during film formation and the macroscopic molecular alignment was demonstrated by taking the process-temperature-dependent properties of the films into consideration. The molecular tilting angle with respect to the column axis was studied by measuring the optic axis direction of the fabricated films and was similar to that of the single crystal. It is considered that despite the non-equilibrium solution process fabrication, highly ordered molecular stacking structure, which is similar to the single crystal, can be obtained in the fabricated films by controlling process temperature.

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References

- [1] G. H. Heilmeier, L. A. Zanoni, Surface studies of α -copper phthalocyanine films, J. Phys. Chem. Solids. 25 (1964) 603-611.
- [2] K. Kudo, M. Yamashita, T. Moriizumi, Field Effect Measurement of Organic Dye Films, Jpn. J. Appl. Phys. 23 (1984) 130.
- [3] C. W. Tang, Two-layer organic photovoltaic cell, Appl. Phys. Lett. 48 (1986) 183-185.
- [4] H. Ebata, T. Izawa, E. Miyazaki, K. Takimiya, M. Ikeda, H. Kuwabara, T. Yui, Highly Soluble [1]Benzothieno[3,2-b]benzothiophene (BTBT) Derivatives for High-Performance, Solution-Processed Organic Field-Effect Transistors, J. Am. Chem. Soc. 129 (2007) 15732-15733.
- [5] J. Soeda, Y. Hirose, M. Yamagishi, A. Nakao, T. Uemura, K. Nakayama, M. Uno, Y. Nakazawa, K. Takimiya, J. Takeya, Solution-Crystallized Organic Field-Effect Transistors with Charge-Acceptor Layers: High-Mobility and Low-Threshold-Voltage Operation in Air, Adv. Mater. 23 (2011) 3309-3314.
- [6] H. Minemawari, T. Yamada, H. Matsui, J. Tsutsumi, S. Haas, R. Chiba, R. Kumai, T. Hasegawa, Inkjet printing of single-crystal films, Nature 475 (2011) 364-367.
- [7] H. Matsui, D. Kumaki, E. Takahashi, K. Takimiya, S. Tokito, T. Hasegawa,

Correlation between interdomain carrier hopping and apparent mobility in polycrystalline organic transistors as investigated by electron spin resonance, *Phys. Rev. B* 85 (2012) 035308.

[8] W. Pisula, A. Menon, M. Stepputat, I. Lieberwirth, U. Kolb, A. Tracz, H. Sirringhaus, T. Pakula, K. Müllen, A Zone-Casting Technique for Device Fabrication of Field-Effect Transistors Based on Discotic Hexa-peri-hexabenzocoronene, *Adv. Mater.* 17 (2005) 684-689.

[9] Y. Diao, B. C-K. Tee, G. Giri, J. Xu, D. H. Kim, H. A. Becerril, R. M. Stolenberg, T. H. Lee, G. Xue, S. C. B. Mannsfeld, Z. Bao, Solution coating of large-area organic semiconductor thin films with aligned single-crystalline domains, *Nat. Mater.* 12 (2013) 665-671.

[10] Y. Yuan, G. Giri, A. L. Ayzner, A. P. Zoombelt, S. C. B. Mannsfeld, J. Chen, D. Nordlund, M. F. Toney, J. Huang, Z. Bao, Ultra-high mobility transparent organic thin film transistors grown by an off-centre spin-coating method, *Nat. Commun.* 5 (2014) 3005.

[11] C. Müller, M. Aghamohammadi, S. Himmelberger, P. Sonar, M. Garriga, A. Salleo, M. Campoy-Quiles, One-Step Macroscopic Alignment of Conjugated Polymer Systems by Epitaxial Crystallization during Spin-Coating, *Adv. Funct. Mater.* 23 (2013)

2368-2377.

[12] M. O'Neil, S. M. Kelly, Ordered Materials for Organic Electronics and Photonics, *Adv. Mater.* 23 (2011) 566-584.

[13] H. Iino, J. Hanna, Availability of Liquid Crystallinity in Solution Processing for Polycrystalline Thin Films, *Adv. Mater.* 23 (2011) 1748-1751.

[14] M. J. Cook, S. J. Cracknell, K. J. Harrison, Liquid-crystalline zinc and nickel 1,4,8,11,15,18,22,25-octaalkylphthalocyaninates: beneficial effect of the zinc ion on mesophase stabilities, *J. Mater. Chem.* 1 (1991) 703-704.

[15] J. C. Swarts, E. H. G. Langner, N. Krokeide-Hove, M. J. Cook, Synthesis and electrochemical characterisation of some long chain 1,4,8,11,15,18,22,25-octa-alkylated metal-free and zinc phthalocyanines possessing discotic liquid crystalline properties, *J. Mater. Chem.* 11 (2001) 434-443.

[16] Y. Miyake, Y. Shiraiwa, K. Okada, H. Monobe, T. Hori, N. Yamasaki, H. Yoshida, M. J. Cook, A. Fujii, M. Ozaki, Y. Shimizu, High Carrier Mobility up to $1.4 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ in Non-Peripheral Octahexyl Phthalocyanine, *Appl. Phys. Express* 4 (2011) 021604.

[17] Q.-D. Dao, T. Hori, K. Fukumura, T. Masuda, T. Kamikado, A. Fujii, Y. Shimizu, M. Ozaki, Effects of processing additives on nanoscale phase separation, crystallization and photovoltaic performance of solar cells based on mesogenic phthalocyanine, *Org.*

Electron. 14 (2013) 2628-2634.

[18] C. W. Sele, B. K. C. Kjellander, B. Niesen, M. J. Thornton, J. B. P. H. van der Putten, K. Myny, H. J. Wondergem, A. Moser, R. Resel, A. J. J. M. van Breemen, N. van Aerle, P. Heremans, J. E. Anthony, G. H. Gelinck, Controlled Deposition of Highly Ordered Soluble Acene Thin Films: Effect of Morphology and Crystal Orientation on Transistor Performance, *Adv. Mater.* 21 (2009) 4926-4931.

[19] I. Chambrier, M. J. Cook, M. Helliwell, A. K. Powell, X-Ray crystal structure of a mesogenic octa-substituted phthalocyanine, *J. Chem. Soc., Chem. Comm.* (1992) 444-445.

[20] M. Yoneya, T. Makabe, A. Miyamoto, Y. Shimizu, Y. Miyake, H. Yoshida, A. Fujii, M. Ozaki, Tilt orientationally disordered hexagonal columnar phase of phthalocyanine discotic liquid crystals, *Phys. Rev. E* 89 (2014) 062505.

Figure captions

Fig. 1. Molecular structure of C6PcH₂.

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.

Fig. 3. X-ray diffraction patterns of the fabricated C6PcH₂ films. (a, b) Patterns by θ -2 θ scan. (c) Patterns by scanning tilting angle χ . The diffraction angle θ was set to the peak by first-order diffraction.

Fig. 4. Polarized absorption spectra of the C6PcH₂ films fabricated with the process temperature of 150 °C. The incident light was polarized parallel (black line) or perpendicular (red line) to the crack direction.

Fig. 5. (a) Measurement system for determining the molecular tilting angles. (b) Measured and calculated tilting angle dependence of transmitted light intensity for the C6PcH₂ film fabricated with the process temperature of 150 °C.

Figure 1

Figure 2

Figure 3

(a)

(b)

(c)

Figure 4

Figure 5