

Epitaxial growth of mesogenic tetrabenzotriazaporphyrin in freezing process from supercooled liquid crystal state

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Abstract

Molecularly oriented thin films of 1,4,8,11,15,18,22,25-octahexyltetrabenzotriazaporphyrin (C6TBTAPH₂) have been fabricated by the contact freezing method with a seed crystal. By dropping a seed crystal of C6TBTAPH₂ or the analogue molecule, 1,4,8,11,15,18,22,25-octahexylphthalocyanine, onto the C6TBTAPH₂ thin film at supercooled liquid crystal state, the homo- or hetero-epitaxial growth spontaneously occurred, respectively. The different crystal structures in the thin films were confirmed by grazing-incidence wide-angle X-ray scattering technique.

1. Introduction

Organic semiconductors have attracted much interest because of their unique properties, such as flexibility and light weight [1-3]. Organic semiconductor thin films fabricated by solution-processing techniques, such as spin-coating method, tend to be polycrystalline involved with many grain boundaries, which interrupt the carrier transport in the thin films [4]. To fabricate highly-ordered crystalline thin films, many solution-processing techniques were proposed. We also recently reported on the molecular alignment of a mesogenic phthalocyanine, 1,4,8,11,15,18,22,25-octahexylphthalocyanine (C6PcH₂), by contact freezing method [5,6].

Contact freezing is a phase transition phenomenon, which is a crystallization begun by giving a stimulation to a substance at the supercooled state [7]. C6PcH₂ exhibits the supercooled LC state between 139 and 161 °C, and the typical contact freezing of C6PcH₂ was demonstrated by bringing a room-temperature metal blade into contact with the thin film at 160 °C [5]. An analogue molecule of C6PcH₂, 1,4,8,11,15,18,22,25-octahexyltetrabenzotriazaporphyrin (C6TBTAPH₂), is a promising donor material for bulk-heterojunction organic solar cells [8], C6TBTAPH₂ also exhibits the supercooled LC state [9], and the contact freezing could be observed.

Recently, we reported on a homo-epitaxial growth in the bar-coating method with seed crystals, which were set around the initial position of the coating bar [10], and demonstrated

the selective crystal growth depending on the crystal polymorphs of the seed crystals. In this study, molecularly oriented thin films of C6TBTAPH₂ were fabricated by the contact freezing method with a seed crystal instead of the metal blade contact, and the molecular orientation of C6TBTAPH₂ were discussed.

2. Experimental

C6TBTAPH₂ was dissolved in toluene at a concentration of 40 g/L, and the solution was spin-coated onto a cleaned glass substrate at 500 rpm for 60 s under nitrogen atmosphere. The spin-coated thin film was mounted on a hot plate and heated to a LC temperature of 155 °C at a rate of 20 °C/min, then cooled to a supercooled LC temperature of 149 °C at a rate of 5 °C/min. At the supercooled LC temperature, the contact freezing was carried out by dropping a needle-shape β -type seed crystal of C6TBTAPH₂ or C6PcH₂ onto the thin film at the supercooled LC state. After completing the freezing, the thin film on the substrate was cooled to room temperature.

The thin films were observed using a polarized optical microscope (Nikon Eclipse E600POL) equipped with a hot stage (Linkam LTS-350). The optical anisotropic properties and optical axis directions of the thin films were clarified by measuring the polarized optical absorption spectra.

The crystal structure and molecular orientation in the thin film were determined by a GIWAXS measurement system using a Rigaku FR-E X-ray diffractometer with a Rigaku R-Axis IV 2D detector. The GIWAXS measurements were carried out when the directions of the incident X-ray were parallel and perpendicular to the crystal growth direction.

3. Results and discussion

The contact freezing phenomenon actually took place by dropping the needle-shape seed crystal of C6TBTAPH₂ or C6PcH₂ onto the C6TBTAPH₂ thin film at the supercooled LC state. Observing at the position where the seed crystal was dropped, the seed crystal remained at the center of the micrograph, and the radial trace of the crystal growth from the seed crystal can be seen. At a distance of about 1 cm away from the dropped seed crystal, the extinction and diagonal positions can be clearly recognized.

To clarify the molecular packing structures in the thin films, the XRD measurements were carried out using the GI-WAXS technique. Figures 1 and 2 show the XRD patterns of the C6BTAPH₂ thin films fabricated with the seed crystals of C6BTAPH₂ and C6PcH₂, respectively. The direction of the incident X-ray was parallel to the crystal growth direction in Figs. 1(a) and 2(a), whereas that was perpendicular in Figs. 1(b) and 2(b). Comparing the XRD images in Figs. 1 and 2, the spot-like patterns were completely different each other. Therefore, it is noted that the C6BTAPH₂ thin films were based on the different crystal structures.

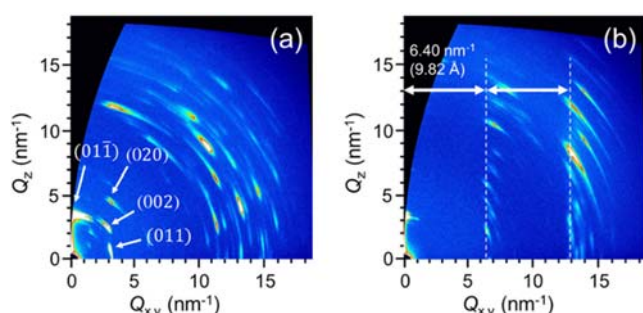


Fig. 1 XRD patterns of the C6BTAPH₂ thin film at room temperature after contact freezing. The C6BTAPH₂ thin film was fabricated by dropping the C6BTAPH₂ seed crystal onto the thin film at supercooled state. The direction of the incident X-ray was parallel to that of crystal growth in (a), and was perpendicular in (b).

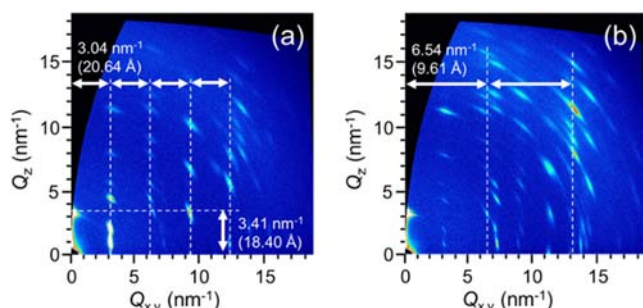


Fig. 2 XRD patterns of the C6BTAPH₂ thin film at room temperature after contact freezing. The C6BTAPH₂ thin film was fabricated by dropping the C6PcH₂ seed crystal onto the thin film at supercooled state. The direction of the incident X-ray was parallel to that of crystal growth in (a), and was perpendicular in (b).

The diffraction peaks in Fig. 1 correspond to the lattice spacings of the β -type C6BTAPH₂ crystal, which were calculated with the lattice parameters of the β -type C6BTAPH₂ single crystal [11]. The (01 $\bar{1}$) plane of β -type C6BTAPH₂ crystal was parallel to the substrate plane, and the crystal structure of the C6BTAPH₂ thin film was same as that of the β -type C6BTAPH₂ seed crystal and the column axis (a axis) was oriented along the crystal growth direction. Thus, the homo-epitaxial growth for C6BTAPH₂ and uniaxial orientation in the thin film with the β -type crystal structure were confirmed.

Although the diffraction peaks were also detected in Fig. 2, these peaks never coincided with the lattice spacing of the β -type C6BTAPH₂ crystal. Therefore, it is suggested that an unidentified crystal structure for C6BTAPH₂, which is called γ -type here, was formed in the thin film. The lattice spacings calculated from the XRD patterns of the γ -type C6BTAPH₂ thin film coincided with those of the β -type C6PcH₂ seed crystal, namely, it is suggested that the γ -type crystal structure of C6BTAPH₂ was similar to the β -type crystal structure of C6PcH₂. Thus, the hetero-epitaxial growth from the β -type C6PcH₂ seed crystal and uniaxial orientation in the thin film were realized.

4. Conclusions

The molecularly oriented thin films of C6BTAPH₂ were fabricated by the contact freezing method with a seed crystal. By dropping C6BTAPH₂ or C6PcH₂ seed crystal onto the thin film at supercooled state, the homo- or hetero-epitaxial growth spontaneously occurred, respectively, and the C6BTAPH₂ thin films with the molecular packing structure obeying the seed crystal were selectively obtained.

Acknowledgements

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References

- [1] C. D. Dimitrakopoulos and P. R. L. Malenfant, *Adv. Mater.* **14**, 99 (2002).
- [2] C. J. Brabec, N. S. Sariciftci, and J. C. Hummelen, *Adv. Funct. Mater.* **11**, 15 (2001).
- [3] D. Tobjörk and R. Österbacka, *Adv. Mater.* **23**, 1935 (2011).
- [4] H. Matsui, D. Kumaki, E. Takahashi, K. Takimiya, S. Tokito, and T. Hasegawa, *Phys. Rev. B* **85**, 035308 (2012).
- [5] M. F. Ramanarivo, T. Higashi, M. Ohmori, K. Sudoh, A. Fujii, and M. Ozaki, *Appl. Phys. Express* **9**, 061601 (2016).
- [6] T. Kitagawa, M. F. Ramanarivo, A. Fujii, and M. Ozaki, *Jpn. J. Appl. Phys.* **57**, 04FL09M (2018).
- [7] L. A. L. Moreno, O. Stetzer, and U. Lohmann, *Atmos. Chem. Phys.* **13**, 9745 (2013).
- [8] Q. D. Dao, L. S. Vargas, T. Higashi, M. Ohmori, H. Itani, A. Fujii, Y. Shimizu, and M. Ozaki, *Org. Electron.* **23**, 44 (2015).
- [9] Q. D. Dao, K. Watanabe, H. Itani, L. S. Vargas, A. Fujii, Y. Shimizu, and M. Ozaki, *Chem. Lett.* **43**, 1761 (2014).
- [10] M. Nakatani, M. Ohmori, S. Nagano, A. Fujii, and M. Ozaki, *Org. Electron.* **62**, 241 (2018).
- [11] M. Ohmori, C. Nakano, A. Fujii, Y. Shimizu, and M. Ozaki, *J. Cryst. Growth* **468**, 804 (2017).