

Fabrication of Single-Crystalline Thin-Film Utilizing Liquid-Crystalline Alkyl-Substituted Phthalocyanine

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Abstract

Fabrication of single crystalline thin films utilizing an organic semiconductor material, liquid crystalline (LC) phthalocyanine, 1,4,8,11,15,18,22,25-octahexylphthalocyanine (C6PcH₂), which demonstrates a high ambipolar mobility and is promising as a donor material for organic solar cells, have been carried out. Three fabrication methods have been proposed by taking the thermotropic LC properties, lyotropic LC properties or crystal polymorphism into consideration, the optical and electrical properties of the single crystalline thin film have been investigated, and the crystal growth mechanisms have been discussed.

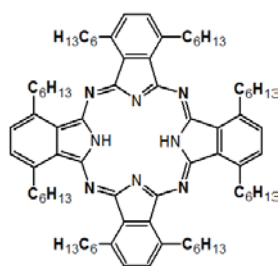


Fig. 1 Molecular structure of C6PcH₂

1. Solvent vapor effects based on solution-mediated polymorphic transformation

Solvent vapor treatment to spin-coated films of a polymorphic C6PcH₂, the molecular structure of which is shown in Fig. 1, was effective for the solution-mediated polymorphic transformation [1-3]. Growth of the single crystalline films via redissolving organic films under solvent vapor was revealed by in-situ microscopic observations of the films as shown in Fig. 6.

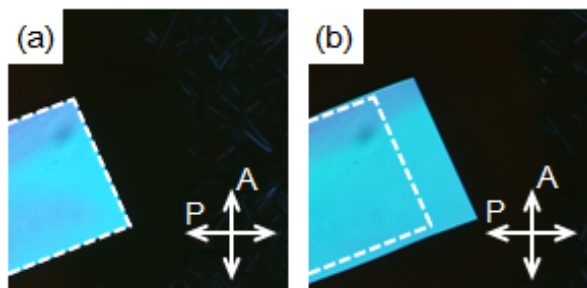


Fig. 2 Polarizing micrographs of film. (b) was taken 10 min after the state of (a).

The X-ray diffraction measurement of the films after exposing to solvent vapor indicated the phase transition between the polymorphs. The crystal growth axis was clarified by measuring the crystal orientation in the grown monodomain film. The mechanism of the crystal growth based on the solution-mediated polymorphic transformation was discussed in terms of the different solubility for each crystal phase.

2. Uniaxially oriented film growth by bar-coating technique

Bar-coating technique, which is a simple solution process, has been adopted as the second method for the uniaxially oriented thin films of C6PcH₂ [4]. The molecular orientation and molecular steps in the thin film were observed by polarized spectroscopy and atomic force microscopy, respectively.

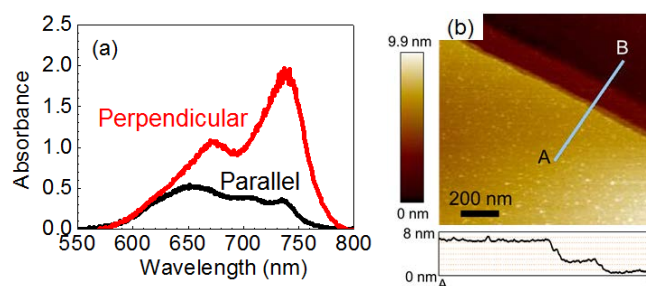


Fig. 3 (a) Polarized absorption spectra of the bar-coating film. The incident light was parallel (black line) or perpendicular (red line) to the film growth direction. (b) AFM image and surface profile of the bar-coating film. The profile corresponds to the white line in the image.

The three-dimensional molecular packing structure in the thin film was investigated by the grazing incidence wide-angle X-ray scattering technique with in-plane sample rotation. The measured X-ray diffraction patterns were reproduced by a simulation based on the lattice parameters of the C6PcH₂ single crystal. The three-dimensional molecular packing structure of the thin film was found to match the single crystal structure.

3. Crystal growth utilizing freeze process from super-cooled LC state

The third method has been proposed for the uniaxial crystal growth after the wet-processed fabrication of the C6PcH₂

thin films. It consists of applying a geometrically linear thermal stimulation to a supercooled state of C6PcH₂, which is shown in Fig. 4 [5, 6].

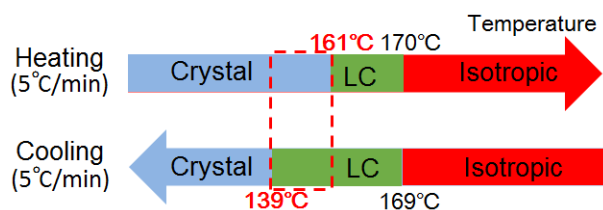


Fig. 4 Phase transition temperature of C6PcH₂ determined by DSC.

The thin-film showed the highly ordered molecular stacking structure and uniaxial alignment over a macroscopic scale. The explanation for the mechanism of the crystal growth has been suggested by taking into account of the temperature range of the crystal growth and hysteresis property of C6PcH₂ in the phase transition.

Acknowledgements

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References

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