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High vertical carrier mobility in the nanofiber films of a phthalocyanine derivative and its application to vertical-type transistors

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ABSTRACT

A self-assembled nanofiber film of octabutoxy-phthalocyanine ($H_2P_COC_4$) was prepared by a simple spin-coating method with a mixed solvent. This film indicated a high vertical hole mobility up to 0.12 $cm^2\ V^{-1}\ s^{-1}$ when the nanofiber structure is formed from a mixed solvent of chloroform and *o*-dichlorobenzene. The high vertical mobility is attributed to the unique crystal structure of $H_2P_COC_4$ and molecular arrangement in the fiber film. Quantum chemical calculations reveal that the crystal structure of $H_2P_COC_4$ enables two-dimensional carrier transport that is advantageous for the vertical transport. The nanofiber films were applied to vertical-type organic transistors, resulting in higher output current compared to a non-structured film.

1. Introduction

Research efforts to improve carrier mobility of organic semiconductors have been made in terms of molecular design, crystal growth, and molecular orientation control. In particular, lateral carrier mobility in organic field effect transistors (OFETs) has been extensively enhanced, and very high values exceeding 10 $cm^2\ V^{-1}\ s^{-1}$ have been reported [1–3]. Carrier transport in the OFETs occurs at the interface between the organic semiconductor and insulating layer, and carriers flow along the substrate surface. In contrast, in organic solar cells (OSCs), organic light emitting diodes (OLEDs), and vertical-type organic transistors, carriers flow perpendicularly to the substrates. The vertical carrier mobilities are therefore an important influence on their performance; nevertheless, they generally remain on the order of 10^{-5}–10^{-3} $cm^2\ V^{-1}\ s^{-1}$, which is much lower than OFET mobilities. Such low vertical mobilities require ultra-thin films around 100 nm to maintain electrical conductivity, which makes mass production processes more difficult. Therefore, high vertical mobility rivaling OFET mobility is required for a major breakthrough in the field of organic electronics.

In recent studies, self-assembled nanostructures such as liquid crystal columns, nanorods, and nanofibers have been utilized in organic electronic devices [4–6]. The molecular orientation to the substrates strongly affects the device performance because charge carriers generally move toward π-π stacks; therefore, face-on orientation is especially important for vertical carrier transport. Feng and co-workers estimated that a defect-free self-assembled structure of discotic liquid crystal columns could lead to a theoretical mobility of 15.9 $cm^2\ V^{-1}\ s^{-1}$ along the column axis based on quantum chemical calculations [7]. The self-assembly of phthalocyanine derivatives has recently attracted research interest [8–10]. A non-peripherally alkyl-substituted phthalocyanine, C_6PcH_2, indicates a discotic liquid crystal phase and high vertical mobility up to 1.4 $cm^2\ V^{-1}\ s^{-1}$ with a thick-film condition (12.5 μm) [11]. However, such preferable liquid-crystal structure is not formed in a thin film below 1 μm, resulting in worse vertical mobility. In addition, one-dimensional columns are not ideal for vertical transport because some defects derived from molecular fluctuations or grain boundaries would critically disturb carrier transport. Two or three-dimensional carrier transport is desirable to improve vertical carrier mobility.

Among various phthalocyanine derivatives, it has been reported that non-peripherally octa (alkoxy)-substituted phthalocyanines form self-assembled nanostructures such as nanowires and nanoribbons by solvent evaporation [12,13]. The details of the self-assembled fiber structure and single crystal structure of 1,4,8,11,15,18,22,25-octabutoxy-29H, 31H-phthalocyanine ($H_2P_COC_4$) (Fig. 1a) have been previously investigated. Gao and co-workers reported that $H_2P_COC_4$ has a distorted molecular structure with a saddle conformation (Fig. 1b) and strong π-π interaction between the neighboring molecules due to a short distance between two overlapped isoindole units [14]. $H_2P_COC_4$ therefore has a great potential for organic semiconductor materials; however, the nanofiber crystals have thus far been prepared by slow solvent evaporation, and thin-film preparation and electrical properties such as carrier mobility have not yet been reported.

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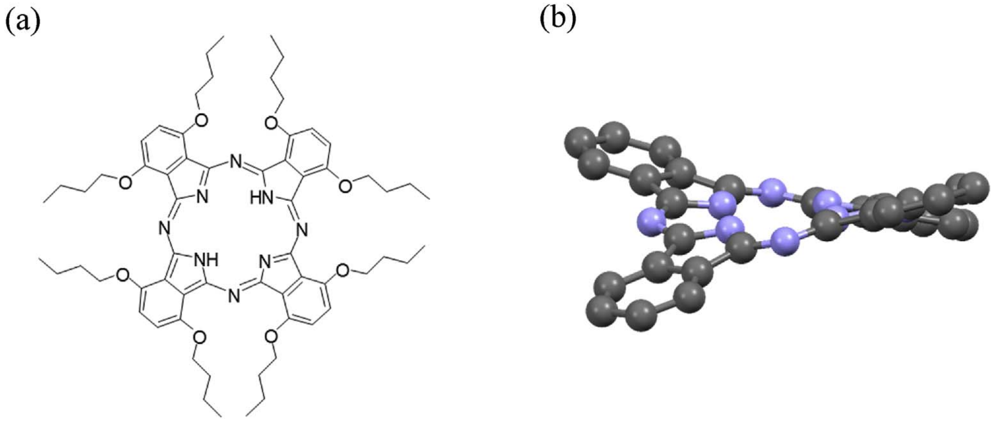

Fig. 1. (a) Chemical structure of $H_2P_COC_4$, (b) side view of its stereostructure (alkoxyl side-chains are omitted).

In this study, we focus on the self-assembly character and the unique single crystal structure of $H_2P_COC_4$ in order to improve the vertical carrier mobility. Self-assembled nanofiber crystals of $H_2P_COC_4$ were prepared by a simple spin-coating method with a mixed solvent, giving a macroscopically uniform film. The vertical hole mobility was measured by the space charge limited current (SCLC) technique, and the relationship between the vertical mobility and the crystal structure or molecular orientation on the substrate was discussed with using quantum-chemical calculations. Furthermore, the nanofiber films of $H_2P_COC_4$ were applied to the metal base organic transistors (MBOTs), which is one of the vertical-type organic transistors.

2. Material and methods

Indium tin oxide (ITO) patterned glass substrates were cleaned by rubbing with acetone soaked wipes, and sonicating in acetone and isopropanol. The washed substrates were exposed to boiling isopropanol and treated with a UV-O_3 cleaner (Filgen, UV253V8). A hole-only device for space charge limited current (SCLC) technique was composed of [glass/ITO/MoO_3 (1 nm)/$H_2P_COC_4$/MoO_3 (1 nm)/Al (100 nm)]. The existence of MoO_3 underlayer after spin-coating was confirmed by comparing AFM images of a glass substrate, MoO_3 (1 nm) on a glass, and that after spin-coating with chloroform (Supporting Information Fig. S1). The granular structure of MoO_3 was observed even after spin-coating, indicating at least there exists the MoO_3 layer on the substrate. MoO_3 and Al were deposited by thermal vacuum evaporation through a shadow mask under a pressure of $\sim 10^{-4}$ Pa. The active area was 4 mm^2. A spin-coated film of $H_2P_COC_4$ purchased from Sigma-Aldrich was prepared from 30 to 50 mg mL^{-1} chloroform solution. A mixed solvent containing chloroform and *o*-dichlorobenzene (*o*-DCB) was also used. The volume ratio of *o*-DCB was 1% and 10%. The film thickness was measured with a surface profiler (Bruker, Dektak XT).

p-type metal-base organic transistors (MBOTs) were fabricated using $H_2P_COC_4$ as an emitter layer and copper phthalocyanine (CuPc) as a collector layer. The device structure was [ITO (collector)/CuPc (100 nm)/Al (15 nm, base)/PEDOT:PSS/$H_2P_COC_4$/MoO_3 (2 nm)/Au (30 nm, emitter)]. CuPc, MoO_3, Al, and Au were deposited by thermal vacuum evaporation. The poly (3,4-ethylenedioxythiophene):poly (4-styrenesulfonate) (PEDOT:PSS) was spin-coated on the Al base electrode to protect the under layers from spin-coating of the upper $H_2P_COC_4$ layer. The $H_2P_COC_4$ film was spin-coated with the same conditions as above. After deposition of the Al base electrode, the substrate was annealed at 150 °C for 1 h in air [15].

Current-voltage curves of hole-only devices and MBOTs were measured with a semiconductor parameter analyzer (Agilent 4155C) in a nitrogen-filled glove box. The film surface morphology was observed by an atomic force microscope (AFM, Bruker, Dimension Icon) with a tapping mode. The thin-film crystal structure was investigated by an X-ray diffractometer (Rigaku, SmartLab) with out-of-plane configuration and Cu Kα radiation ($\lambda = 1.5418$ Å).

3. Results and discussion

The surface morphology of the $H_2P_COC_4$ films observed by AFM is shown in Fig. 2. The films spin-coated with chloroform solution (0% *o*-DCB) showed an irregularly-aggregated structure, but there was no crystalline structure. Increasing $H_2P_COC_4$ concentration (from 30 to 50 mg mL^{-1}) gave a larger film thickness, but no structural change. In contrast, the films spin-coated from the mixed solvent containing 10% *o*-DCB clearly showed nanofiber structure. The nanofibers were several hundreds nm to 1 μm in width, and several microns in length, forming a continuous fiber-network. The widths of the fibers becomes larger for a higher-concentration solution. This result indicates that growth speed of the fibers is increased by higher $H_2P_COC_4$ concentration. The effect of *o*-DCB is attributed to the boiling point, which is an important factor to control evaporation speed in the spin-coating process. *o*-DCB with higher boiling point (b.p. 181 °C) compared to chloroform (b.p. 61 °C) gives slow evaporation, facilitating crystal growth during spin-coating. Other *o*-DCB ratios (from 1% to 50%) were also investigated. The 1% *o*-DCB films did not show any structural change compared to the chloroform films (Supporting Information Fig. S2). The 50% *o*-DCB solution could not form any films because the solution was completely spun out during the spin-coating process. The 10% *o*-DCB solution had a suitable balance between solvent evaporation and crystal growth, resulting in formation of the fiber film. UV/vis spectra of the H_2PcOC_4 films are indicated in the Supporting Information (Fig. S3). The fibrous films showed broader peaks from 600 nm to 900 nm compared to the non-fibrous films, suggesting enhancement of film crystallinity or change of stacking mode.

The crystallinity and molecular orientation of the $H_2P_COC_4$ film were investigated by X-ray diffraction measurements in the out-of-plane configuration (Fig. 3). The interplanar distance *d* evaluated from the Bragg equation corresponds to the distance between crystallographic planes lying parallel to the substrate [16,17]. The films spin-coated without *o*-DCB showed only one peak at 5.5° ($d = 16.0$ Å) assigned to the (001) plane, indicating completely edge-on orientation where the molecular plane is perpendicular to the substrates (Fig. 4a). This peak pattern is not affected by the solution concentration. In contrast, the fiber films from the mixed solvent showed additional peaks at 8.0° and 24.0° ($d = 11.0$ Å, 3.7 Å) assigned to (110) and (332) plane, respectively. The (332) peak in the out-of-plane configuration corresponds to the distance among phthalocyanine stacks lying parallel to the substrate surface as shown in Fig. 4(b). Therefore, we concluded that the H_2PcOC_4 molecules had face-on orientation in the fibrous films, where π–π interactions exist along both *a* and *b* axes with a short distance (3.351–4.019 Å) between two overlapped isoindole units in an alternating manner. When the fibrous films are formed with the mixed