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Magnetic-field-induced enhancement of crystallinity and field-effect mobilities in phthalocyanine thin films

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Organic semiconductor thin films were fabricated by thermal deposition of free-base and metal phthalocyanines under a static magnetic field. A vertical magnetic field enhanced the crystallinity of the edge-on orientation of the phthalocyanine discs, whereas a horizontal magnetic field had a minimal effect on the crystallinity. The major factor for the orientation change is attributed to the diamagnetic anisotropies of π -electrons in the phthalocyanine macrocycles. Field-effect transistors of phthalocyanine films fabricated under a vertical magnetic field exhibited better hole mobilities and on-current values with smaller threshold voltages than those of phthalocyanine films fabricated without a magnetic field. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4816244>]

Control of molecular orientation with better crystallinity is important for enhancing the performance of organic semiconducting devices such as organic field-effect transistors (OFETs) and organic solar cells (OSCs).^{1–3} For efficient charge carrier transport, parallel alignment of π -stacked columns of discotic molecules to a substrate surface with high crystallinity is appropriate for OFETs,⁴ whereas homeotropic columnar orientation is preferred for OSCs.⁵ Several methods for improving the crystallinity of organic thin films have been proposed, such as thermal heating of the substrate during deposition, thermal- or solvent-annealing after thin-film fabrication, and surface treatment of the substrate.^{1–4,6–9} However, applying external fields during the thin-film fabrication process might make it possible to control both the orientation and crystallinity of thin films with ease over large areas without a time-consuming and complicated fabrication process.^{10–13} In particular, the use of a magnetic field is a powerful technique for controlling the orientation of various kinds of materials such as carbon nanotubes^{14,15} and liquid crystalline (LC) mesogens.^{16,17} In case of fluidic materials such as LCs and materials in viscous media, a magnetic field is efficient for aligning the materials. However, for solid organic materials without fluidic media, orientation control using a magnetic field is very rare. Furthermore, generation of a strong magnetic field requires large and expensive equipment such as electromagnets and superconducting magnets. Thus, molecules capable of responding to small magnetic fields are required for a simple fabrication process. In this study, we report how the magnetic field affects the orientation and crystallinity of thin films of discotic phthalocyanine (Pc) molecules (Figure 1(a)), by utilizing small permanent magnets with sub-Tesla magnetic flux density. We initially anticipated that a horizontal magnetic field ($H_{//}$, Figure 1(b)) may induce in-plane alignment of π -stacked Pc columns, which would lead to in-plane anisotropic charge

carrier transport. However, no such effect was observed for thin films fabricated under $H_{//}$. In contrast, we found that a vertical magnetic field (H_{\perp} , Figure 1(c)) can enhance crystallinity of the edge-on orientation of Pc molecules, which results in better OFET properties in comparison with thin films fabricated without a magnetic field.

By applying an external magnetic field, a molecule having a magnetic anisotropy ΔK ($= K_{\perp} - K_{//}$, where K_{\perp} and $K_{//}$ are molecular principal susceptibilities perpendicular and parallel to the symmetry axis of the molecule, respectively) is subject to a torque N expressed as follows:

$$N = I\alpha = -m\Delta KB^2 \sin 2\theta, \quad (1)$$

where I , α , m , B , and θ denote moment of inertia, angular acceleration, mass of molecule, magnetic flux density, and angle between molecular symmetry axis and magnetic flux, respectively.¹⁸ When a molecule orients its magnetization easy axis along the direction of the magnetic field, the molecule is stabilized by the free energy gain (ΔU) described as follows:

$$\Delta U = -(1/2)\Delta KB^2. \quad (2)$$

Pc molecules possess D_{4h} symmetry; K_{\perp} and $K_{//}$ are the in-plane and out-of-plane susceptibilities of the Pc disc, respectively (Figure 1(a)). According to previous reports, magnetic anisotropies of free-base (H_2Pc) and diamagnetic metal phthalocyanines (NiPc and ZnPc) possess ΔK in a range of $500\text{--}650 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$ (Table I),¹⁹ which mainly derives from the π -electrons of porphyrazine macrocycles. Copper phthalocyanine (CuPc) possesses an unpaired d -electron on the metal center, in addition to π -electrons. However, the unpaired electron in the $d_{x^2-y^2}$ orbital with D_{4h} symmetry shows quite small magnetic anisotropy, and thus, the ΔK of CuPc ($= 644 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$, Table I)²⁰ is comparable to those of the other diamagnetic Pcs. The positive value of ΔK indicates that Pcs are energetically stable when the disc plane orients parallel to the magnetic field.

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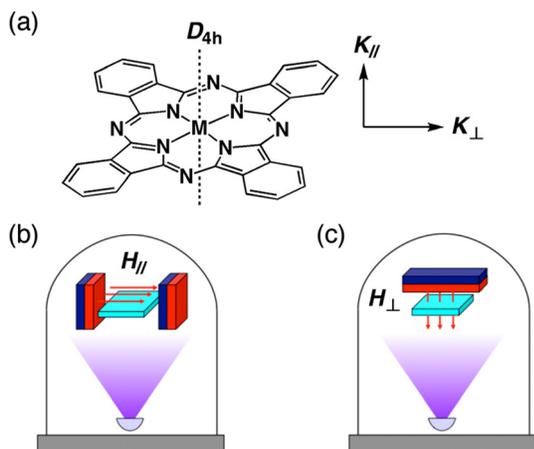


FIG. 1. (a) Molecular structure of metal phthalocyanine, its D_{4h} symmetry axis, and the directions of molecular principal susceptibilities, $K_{//}$ and K_{\perp} . (b) and (c) Schematic illustrations of the experimental setups for thermal deposition of Pcs under horizontal (b) and vertical (c) magnetic fields ($H_{//}$ and H_{\perp} , respectively).

Based on these magnetic anisotropy data, we fabricated CuPc, NiPc, and H_2 Pc thin films under a static magnetic field using neodymium–iron–boron (Nd–Fe–B) permanent magnets. The square-shaped magnets with 4.0 cm on a side and 1.5 cm in thick were placed in a vacuum evaporation chamber in such a way that the magnetic field was applied parallel ($H_{//}$) or perpendicular (H_{\perp}) to the substrate (Figures 1(b) and 1(c), respectively). The magnetic flux density at the substrate surface was 0.35 T for each configuration. The distance between substrate and evaporation source is 20 cm. Prior to the thin-film fabrication, the powder samples of CuPc, NiPc, and H_2 Pc, purchased from Aldrich Co. Ltd., were purified

TABLE I. Magnetic anisotropies (in $10^{-6} \text{ cm}^3 \text{ mol}^{-1}$) of H_2 Pc, NiPc, ZnPc, and CuPc.

| | ΔK | $K_{//}$ | K_{\perp} | Ref. |
|----------|------------|----------|-------------|------|
| H_2 Pc | 610 | -751 | -141 | 19 |
| NiPc | 505 | -565 | -60 | 19 |
| ZnPc | 647 | -851 | -204 | 19 |
| CuPc | 644 | No data | No data | 20 |

twice by thermal sublimation in vacuum. The evaporation rate, substrate temperature, and vacuum level were 0.2 \AA s^{-1} , $25 \text{ }^\circ\text{C}$, and $5.0 \times 10^{-4} \text{ Pa}$, respectively, and the film thicknesses were fixed at 50 nm.

Figure 2(a) shows out-of-plane X-ray diffraction (XRD) patterns of CuPc thin films on glass substrates under no magnetic field (no H), $H_{//}$, and H_{\perp} . A diffraction peak assigned as α -CuPc (200) was observed at 2θ of 6.8° ($d = 12.8 \text{ \AA}$) for all the magnetic field conditions,²¹ indicating that CuPc molecules are deposited with an edge-on orientation. However, the diffraction intensity was obviously different: The sample fabricated under H_{\perp} displayed 1.5-times stronger diffraction intensity than that fabricated under no H and $H_{//}$. A similar tendency was observed for the diamagnetic NiPc and H_2 Pc thin films (Figures 2(b) and 2(c), respectively), where H_{\perp} resulted in 1.4–1.5-times stronger intensity of the (200) diffraction peaks in comparison with no H and $H_{//}$. These observations clearly indicate that the crystallinity of the edge-on orientation of Pcs is enhanced by a vertical magnetic field. It is worth noting that the effect of H_{\perp} was observed when CuPc was deposited on an Au-coated substrate. CuPc tends to align with a face-on orientation on metal surfaces.^{22,23}

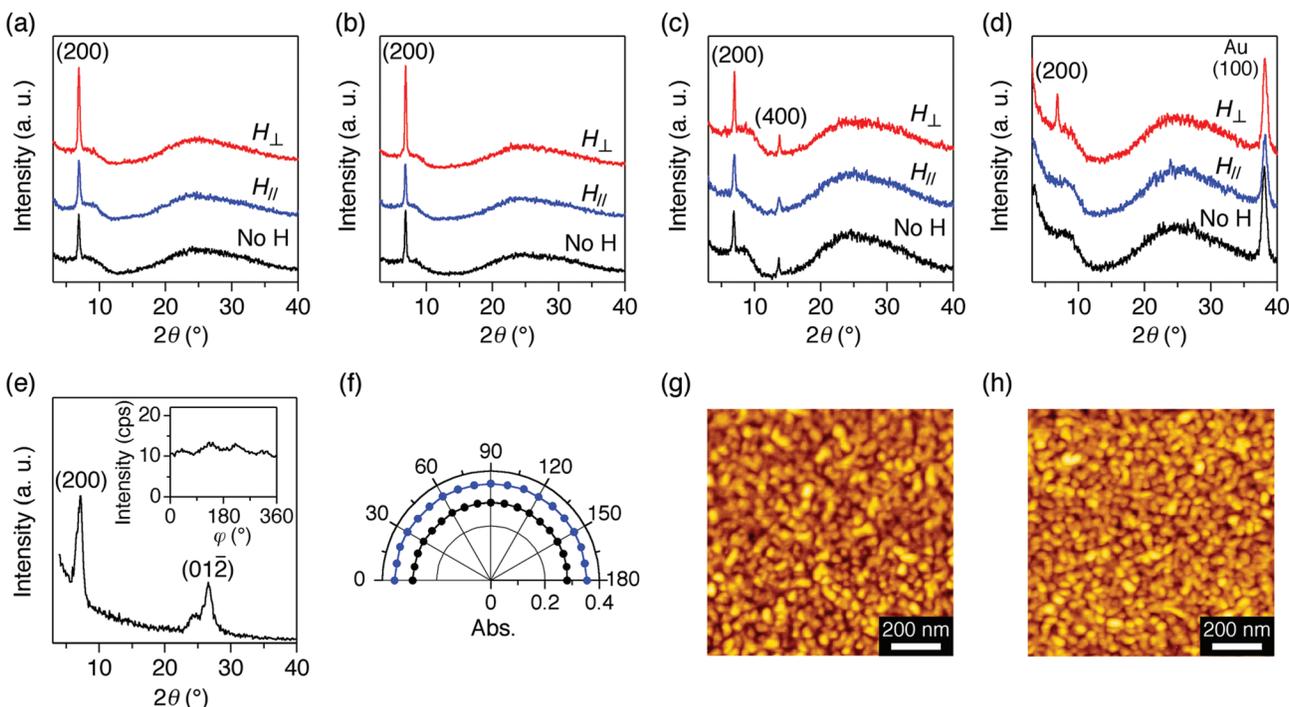


FIG. 2. Out-of-plane XRD patterns of (a) CuPc, (b) NiPc, and (c) H_2 Pc thin films on glass substrates, and (d) CuPc thin films on a Au (10 nm)/glass substrate fabricated under no H (black), $H_{//}$ (blue), and H_{\perp} (red). (e) In-plane XRD pattern by grazing incidence X-ray beam of CuPc thin film on a glass substrate fabricated under $H_{//}$. Inset shows φ -angle dependency of the diffraction intensity at $2\theta = 6.8^\circ$. (f) Polar plots of absorbance at 622 nm , recorded upon rotation of a polarizer every 10° , for CuPc thin films fabricated under no H (black) and $H_{//}$ (blue). AFM images of CuPc thin films on glass substrates fabricated under (g) no H and (h) H_{\perp} . The average grain size and rms roughness are 48 nm and 0.79 nm, respectively, for no H and 55 nm and 0.75 nm, respectively, for H_{\perp} .

However, H_{\perp} partly changed the orientation of CuPc to an edge-on orientation (Figure 2(d)).

The Pc discs tend to align parallel to the magnetic field as a result of the diamagnetic anisotropies of the Pc discs. As shown in Figure 3(a), H_{\perp} induces a rotational motion of Pc discs toward the upstanding direction, leading to the enhanced crystallinity of the edge-on orientation of Pcs. On the other hand, H_{\parallel} imparts in-plane rotational torque to the Pc disc (Figure 3(b)). Initially, we expected that H_{\parallel} would result in a parallel alignment of π -stacked Pc columns by the in-plane rotation. However, the magnetic field used in this study was not strong enough to rotate the Pc discs toward the in-plane direction. In fact, in-plane XRD analysis of the CuPc thin film fabricated under H_{\parallel} showed φ -angle dependencies of the (200) diffraction intensity, but it was negligibly small (Figure 2(e)). Furthermore, polar plots of the absorbance at 622 nm in the polarized absorption spectra of the CuPc thin film fabricated under H_{\parallel} displayed nearly complete semicircles, similar to that of the CuPc thin film fabricated under no H (Figure 2(f)). It is worth noting that, from atomic force microscopy (AFM) images, minimal morphological differences were observed between the CuPc thin films prepared under no H (Figure 2(g)) and those prepared under H_{\perp} (Figure 2(h)). This result clearly indicates that the crystallinity in each grain improves more for thin films fabricated under H_{\perp} than for thin films fabricated under no H .

It was thought that improved crystallinity of CuPc thin films by H_{\perp} may improve the charge transport properties. To address this issue, we fabricated FET devices using CuPc thin films fabricated under a magnetic field. Thus, CuPc films were deposited (film thickness: 15 nm) on a 1,1,1,3,3,3-hexamethyldisilazane (HMDS)-treated SiO_2 (200 nm)/p-Si substrate with and without a magnetic field, and then, the source and drain Au electrodes (50 nm) were deposited onto the CuPc thin films to construct top-contact bottom-gate FET devices with a channel width and length of 0.75 mm and 50 μm , respectively.^{24,25} As shown in Figure 4(a), all the CuPc films displayed an output profile characteristic of p-type FETs, where the drain current (I_d) was linearly enhanced and then saturated as the drain bias voltage (V_d) increased to a negative side under a gate bias voltage (V_g) of -50 V. Obviously, a CuPc thin film fabricated under H_{\perp} ($=0.35$ T) exhibited larger I_d in comparison with that fabricated under no H (Figure 4(a)). The observed I_d value was further increased when H_{\perp} was increased to 0.50 T, where I_d was enhanced fourfold in comparison with that fabricated under no H (Figure 4(a)). The field-effect mobilities (μ_{FET}) for devices under H_{\perp} of 0.35 T and 0.50 T were increased by 1.4 and 2.1 times, respectively, in comparison with that

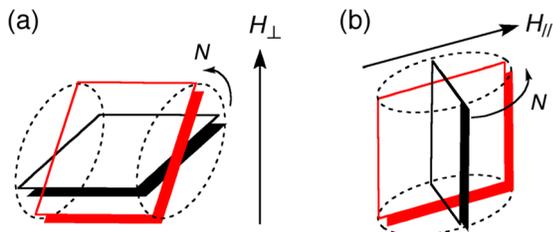


FIG. 3. Schematic representations of the directions of the rotational torque N for the discotic molecules under (a) H_{\perp} and (b) H_{\parallel} .

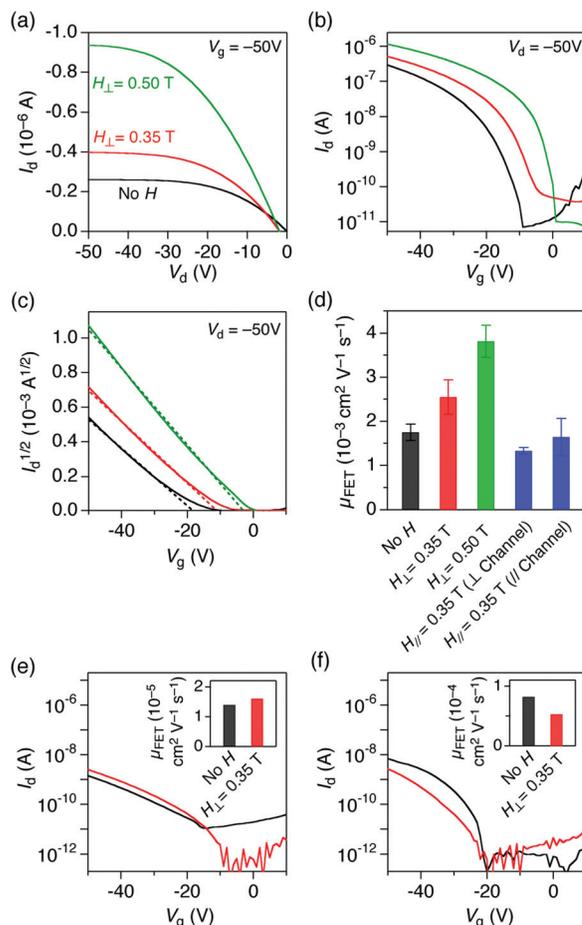


FIG. 4. (a) Output profiles of CuPc thin films fabricated under no H (black), $H_{\perp} = 0.35$ T (red), and $H_{\perp} = 0.5$ T (green) with V_g of -50 V. (b) and (c) Transfer profiles of CuPc thin films fabricated under no H (black), $H_{\perp} = 0.35$ T (red), and $H_{\perp} = 0.5$ T (green) under V_d of -50 V. (d) μ_{FET} of CuPc thin films fabricated under various magnetic field conditions. (e) and (f) Transfer profiles of NiPc and H_2Pc thin films fabricated under no H (black) and $H_{\perp} = 0.35$ T (red) under V_d of -50 V. Insets show μ_{FET} of NiPc and H_2Pc thin films fabricated under no H and $H_{\perp} = 0.35$ T.

fabricated with no H (Figure 4(d) and Table II). Furthermore, both the on-current values at V_g of -50 V (Figure 4(b)) and the threshold voltages (V_{th} , Figure 4(c)) were improved for samples fabricated under H_{\perp} (Table II). Because the size of the grains was identical in the CuPc thin films prepared under no H and H_{\perp} (Figures 2(g) and 2(h)), the enhanced FET properties most likely result from the modified crystallinity of each grain. According to the systematic decrease of V_{th} values for the samples prepared under H_{\perp} , the better crystallinity of CuPc films enhanced not

TABLE II. μ_{FET} , V_{th} , and on-to-off current ratio of CuPc thin films fabricated under no H , H_{\perp} , and H_{\parallel} . The values are average of 3–5 samples. Numeric values in parentheses indicate standard deviations.

| | μ_{FET} ($\times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) | V_{th} (V) | on/off ($\times 10^4$) |
|---|---|------------------------|-----------------------------|
| No H | 1.8(2) | $-19(0)$ | 4.2 |
| $H_{\perp} = 0.35$ T | 2.6(4) | $-11(1)$ | 1.4 |
| $H_{\perp} = 0.5$ T | 3.8(4) | $-2(1)$ | 16 |
| $H_{\parallel} = 0.35$ T (\perp channel) | 1.3(1) | $-18(1)$ | 3.0 |
| $H_{\parallel} = 0.35$ T (\parallel channel) | 1.6(4) | $-13(5)$ | 3.6 |

only the charge carrier mobilities but also charge injection from the electrode. In contrast, the CuPc thin films fabricated under $H_{//}$ exhibited no clear differences in comparison with those fabricated under no H , irrespective of whether the channel direction was parallel or perpendicular to the magnetic field direction (Figure 4(d) and Table II). These results were consistent with the fact that in-plane anisotropy of the molecular orientation was hardly induced by $H_{//}$, as evidenced by in-plane XRD and polarized absorption spectroscopy results (Figures 2(e) and 2(f)). Because the magnetic field is applied only close to the substrate, we consider that H_{\perp} affects the molecules on the substrate surface just after they are deposited, not during they are approaching to the substrate. It is worth noting that NiPc and H₂Pc also showed enhanced crystallinity when fabricated under H_{\perp} (Figures 2(c) and 2(d)). However, thin films of these compounds exhibited very poor FET outputs with the μ_{FET} values in the order of $10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. Furthermore, H_{\perp} resulted in little enhancement in FET properties or even makes it worse (Figures 4(e) and 4(f)).

In summary, applying a vertical magnetic field during the fabrication process of phthalocyanine thin films can induce their edge-on orientation and enhance the film crystallinity, thus improving the charge transport properties. This simple fabrication method is quite useful and widely applicable for enhancing the performance of various kinds of organic semiconducting molecules. Molecules such as pentacene and rubrene in particular, which originally exhibit high field-effect mobilities in OFET devices,^{26,27} may be candidates for the magnetic field-induced orientation. Molecules having large paramagnetic anisotropy will be much more sensitive to magnetic fields.

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