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<th>Journal:</th>
<th>Journal of Materials Chemistry C</th>
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<td>Manuscript ID</td>
<td>TC-COM-07-2021-003547.R2</td>
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<tr>
<td>Article Type:</td>
<td>Communication</td>
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<tr>
<td>Date Submitted by the Author:</td>
<td>08-Sep-2021</td>
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<tr>
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COMMUNICATION

Single crystal field-effect transistor of tetrabenzoporphyrin with one-dimensionally extended columnar packing motif exhibiting efficient charge transport property

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5,15-Bis(triisopropylsilyl)ethynyltetrabenzoporphyrin (TIPS-H2BP) gave one-dimensionally extended columnar packing motif. Single crystal field-effect transistor of TIPS-H2BP exhibited clearly better hole mobility (2.16 cm2 V–1 s–1) than its metal complexes (ca. 0.1 cm2 V–1 s–1), with the efficient charge transports through π–π stacking along tetrabenzoporphyrin units.

The charge transport in organic semiconductors is achieved by the π orbital overlapping of the conjugated molecules along the direction of carrier flow. Therefore, organic semiconducting materials with a rigid and planar π-system have a great potential to provide the suitable packing to increase the π orbital overlap.4–7 Due to the large and rigid π-system, tetrabenzoporphyrins (TBPs) are promising candidates as efficient p-type semiconducting materials.5,6 However, BP itself is hardly soluble in organic solvents, resulting in the difficulty in its direct solution deposition. In addition, the solubility is an important factor not only for the solution-processable device fabrication but also for achieving the large-scale synthesis by conventional organic chemistry together with easy purification by column chromatography. Although these factors, rigidity and solubility, are likely a trade-off relationship, several molecules perfectly satisfy these requirements. For example, 6,13-bis(triisopropylsilyl)pentacene (TIPS-Pen), which is a benchmark compound as an efficient organic semiconducting material, has proven to be quite successful, despite the fact that the pentacene itself is almost insoluble in common organic solvents.7 Taking advantage of the improved solubility by the introduction of TIPSethynyl groups, the solution sharing with a micropillar-patterned blade gave the hole mobility up to 11 cm2 V–1 s–1,8 achieving clearly better hole mobility than pristine pentacene.

For BPs as well, recent synthetic efforts had solved the solubility problem by using “precursor method”, in which a soluble precursor compound, 1,4:8,11:15,18:22,25-tetraethano-29H,31H-tetrabenzo[ b,g,l,q]porphyrin (CP), can be quantitatively converted to BP by a thermally induced retro-Diels-Alder reaction with heating at 150–200 °C for several minutes.6,9 Importantly, the retro-Diels-Alder reaction releases only ethylene molecules as gaseous byproducts. Thus, no purification process is required to obtain pure compounds, if the corresponding precursors are sufficiently pure. The charge-carrier mobility of BP polycrystalline film obtained via precursor method was firstly evaluated by Aramaki, exhibiting the hole mobility of 0.017 cm2 V–1 s–1.10 The hole mobility was then slightly improved to 0.07 cm2 V–1 s–1, while the value was still low.11 Recently, the substituent effect was evaluated to obtain better charge transport property by controlling the packing orientation of BP. It was found that 5,15-bis(triisopropylsilyl)ethynyl)BP (TIPS-H2BP) with reasonable solubility for solution-processed organic thin film transistors formed two types of packing motifs: columnar motif by drop-casting and brickwork motif by dip-coating method.12 The drop-casting films with the columnar motif showed low hole mobility (0.027 cm2 V–1 s–1), although such a columnar motif is also known to exhibit efficient charge transport property. On the other hand, the brickwork motif has two dimensionally extended π-stacking. The maximum hole mobility of dip-coating films reached 1.1 cm2 V–1 s–1, which was approximately 14 times higher than pristine free-base BP (0.07 cm2 V–1 s–1). This disparity in charge transport property derived from different packing motif prepared by drop-casting and dip-coating methods turned our attention to single-crystal field-effect transistors (SCFETs), which are able to unveil the intrinsic charge transport property of organic semiconducting materials due to ordered arrangement of molecules, free of grain boundaries and minimized defects. The obtained maximum hole mobility of TIPS-H2BP in the above report12 implied that functionalized BP...
derivatives could be candidates for efficient organic semiconducting materials. For further structural fine-tuning of BP, the potential of TIPS-H$_2$BP as a simple prototype is necessary to be evaluated by using the single crystal. In this study, single crystals of TIPS-H$_2$BP and its metal complexes were prepared on a substrate, and the molecular orientation in the single crystal was explored in detail. Then, the relationship between the molecular orientation and charge transport property was investigated by preparing SCFETs.

**Fig. 1.** The structure of TIPS-H$_2$BP and its metal complexes employed in this study.

TIPS-H$_2$BP and the zinc(II) and copper(II) complexes (TIPS-ZnBP and TIPS-CuBP) were synthesized by following the previous reports (Fig. 1). Then, their crystals were grown by drop-casting the toluene solution on octadecyltrichlorosilane (OTS) modified Si/SiO$_2$ surface. It was found that slow evaporation of the drop-casted toluene solution gave isolated and thin ribbon-shaped single crystals on Si/SiO$_2$/OTS substrates (Fig. 2). Importantly, the changing of interfacial color in polarized optical microscope (POM) images indicated that they were single crystals. Narrow ribbon-shaped crystals of TIPS-H$_2$BP similar to the case of TIPS-CuBP were also observed. However, out-of-plane X-ray diffraction (XRD) and transmission electron microscopy (TEM) analyses indicated that the molecular orientation in these crystals were the same (vide infra). Indeed, the crystal was grown as the different shape probably because of the slightly different surface energy on a substrate. Here, the order of ease of crystal formation was as follows: TIPS-H$_2$BP > TIPS-ZnBP > TIPS-CuBP. Specifically, single crystals of TIPS-CuBP suitable for SCFETs were hardly obtained on a Si/SiO$_2$/OTS substrate, usually giving a fiber-like structure (Fig. S1).

**Figure 2.** Typical POM images of ribbon-shaped single crystal of (a) TIPS-H$_2$BP, (b) TIPS-ZnBP, and (c) TIPS-CuBP on OTS modified Si/SiO$_2$ substrate. Concentrations for drop-casting of toluene solution: 1.0 mg/ml (TIPS-H$_2$BP and TIPS-CuBP), 0.5 mg/ml (TIPS-ZnBP).

Before examining the molecular orientation of single crystals on a substrate, the bulk single crystal structures for each BP derivative were analyzed in order to establish a referential basis for further discussion. Those single crystals were prepared from toluene solutions, although the X-ray analysis had already been done with single crystals obtained from different solvent system in the previous report. In fact, solvents showed no significant effect on their packing structures. Briefly, a large TIPS-H$_2$BP core (Fig. 3a,b) formed a one-dimensionally extended columnar π-stacking motif with the plane-to-plane distance of BP of ca. 3.3 Å (Fig. 3c). TIPS-H$_2$BP molecules stacked orthogonally in the packing, alternately possessing planar TIPS-H$_2$BP molecule (Fig. 3a) and the one with two TIPSethynyl groups bend from the BP plane sigmoidally (Fig. 3b). It is evident that the well-ordered alignment of TIPS-H$_2$BP facilitates the intermolecular charge transport in the column. BP backbones of TIPS-ZnBP and TIPS-CuBP are similar to the one of TIPS-H$_2$BP. However, molecules in the single crystal form a triad-like structure in which the molecules are stacked orthogonally. In the triad-like structure, TIPS-ZnBP and TIPS-CuBP also have the plane-to-plane distance of ca. 3.3 Å, while the triad units are packed parallel to provide one-dimensional slip-stacked structures. In addition, a planar TIPS-ZnBP or TIPS-CuBP molecule is sandwiched by the respective metal complexes with sigmoidally bend TIPSethynyl groups in the triad-like structure. As the result, a long-range molecular orientation is missing in the cases of TIPS-ZnBP and TIPS-CuBP, in contrast with that observed in TIPS-H$_2$BP.
Fig. 3. (a,b) Single crystal X-ray structure of TIPS-H$_2$BP. Thermal ellipsoids represent 50% probability. Packing structure of (c) TIPS-H$_2$BP, (d) TIPS-ZnBP, and (e) TIPS-CuBP in the crystals obtained from toluene. Hydrogen atoms are omitted for clarity (c–e).

To shed light on the molecular orientation of single crystals on a substrate, out-of-plane XRD analysis was performed (Fig. 4 and Fig. S2). In the case of TIPS-H$_2$BP (Fig. 4a), the intense peaks at 2$\theta$ = 5.16$^\circ$ with a d-spacing of 17.1 Å together with peaks at 2$\theta$ = 6.10$^\circ$ (d-spacing = 14.5 Å) and at 2$\theta$ = 6.22$^\circ$ (d-spacing = 14.2 Å) were well-consistent with the simulated [001], [010], and [011] diffractions of one-dimensional columnar structure (Fig. 3c), respectively, according to the crystallographic data for the bulk crystal. These results support that the one-dimensional columnar packing in parallel to the substrate was grown through $\pi$–$\pi$ stacking direction of TIPS-H$_2$BP. Note that a peak at 4.66$^\circ$, which corresponds to [001] of the brickwork motif, was not observed. Similarly, the peaks at 2$\theta$ = 5.02$^\circ$ (d-spacing = 17.6 Å) and at 2$\theta$ = 5.77$^\circ$ (d-spacing = 15.3 Å) for TIPS-ZnBP are good agreement with the simulated [001] and [010] diffractions of TIPS-ZnBP columnar structure, respectively (Fig. 4b). In the case of TIPS-CuBP, small peaks at 2$\theta$ = 5.03$^\circ$ (d-spacing = 17.6 Å) and at 2$\theta$ = 5.82$^\circ$ (d-spacing = 15.2 Å) which correspond to [001] and [010], respectively, could be observed (Fig. 4c), while the less amount of single-crystals on the substrate resulted in the overall weak peak intensity of XRD pattern. As described above, fiber-like structure also formed on a substrate together with ribbon-shaped crystals (Fig. S1). Rigid $\pi$-systems could form the crystalline nanofibers.21,22 Thus, these crystalline fibers account for the peaks at 2$\theta$ = 4.87$^\circ$ and 2$\theta$ = 5.16$^\circ$ which are not consistent with the simulated patterns of the one-dimensional columnar packing.

Fig. 4. Experimental out-of-plane XRD and simulated powder XRD patterns of (a) TIPS-H$_2$BP, (b) TIPS-ZnBP, and (c) TIPS-CuBP.

In order to confirm the molecular arrangements in the ribbon-shaped crystals, TEM images and their corresponding selected area electron diffraction (SAED) patterns were collected from an individual ribbon-shaped crystal (Fig. 5). The observed bright diffraction spots demonstrated the high-quality of crystallinity. Here, the SAED pattern could be indexed with its single crystal structure, while the SAED patterns for TIPS-H$_2$BP and TIPS-ZnBP are not complete. It was found that the preferred crystal growth directions of TIPS-H$_2$BP, TIPS-ZnBP, and TIPS-CuBP were expected to be [100], [–111], and [–111], respectively (Fig. 3c–e), which are in good agreement with the morphologies predicted through the Bravais–Friedel–Donnay–Harker (BFDH)23–25 method (Fig. 5). Thus, SAED patterns and TEM analysis together with XRD measurement indicated that the growth direction of the ribbon-shaped crystals on the substrate was guided by $\pi$–$\pi$ interactions, creating one-dimensionally extended packing motif as a charge-carrier transport.

Finally, the charge transport property of single crystals was evaluated by fabricating bottom-gate-top-contact organic field-effect transistors using “gold layer gate technique”.26 Briefly, gold source and drain electrodes were placed on the crystals which were grown by drop-casting the toluene solution on Si/SiO$_2$/OTS substrate. The effective channel length and width were measured by microscopy (Fig. S3).

The ribbon-shaped crystals of TIPS-H$_2$BP exhibited an average value of 1.16 cm$^2$ V$^{-1}$ s$^{-1}$ with 15 devices (Fig. 6a,d), giving the maximum hole mobility of 2.16 cm$^2$ V$^{-1}$ s$^{-1}$ with a threshold voltage $V_G$ of 15.6 V and on/off ratio $I_{ON}/I_{OFF}$ of 6.1 x 10$^5$ (Fig. S4). In the previous report, the one-dimensional columnar structure of TIPS-H$_2$BP prepared by drop-casting method exhibited the hole mobility of 0.027 cm$^2$ V$^{-1}$ s$^{-1}$.6 Thus, the maximum hole mobility obtained in this study is approximately 87 times higher than that of the drop-casting one. This result supported that the molecular orientation of TIPS-H$_2$BP is preferable to SCFETs, with the charge transport through $\pi$–$\pi$ stacking of BP units in the one-dimensional column. In addition, the efficient charge transport reflected the feature of single crystals with free of grain boundaries and minimized defects. It should be noted that nearly identical curves were observed after 10 cycles (Fig. S5), suggesting the good bias-stress stability of SCFETs based on ribbon-shaped crystals of TIPS-H$_2$BP. Here, SCFET devices based on TIPS-H$_2$BP often showed the hole carried on operation mode specially for the device which exhibited the high hole mobility (Fig. S4), indicating that the transport channel already formed even without gate bias ($V_G$ = 0 V). This is probably due to the
high hole density of TIPS-H$_2$BP. The holes not only filled the trap states, but also the excess holes became free carriers, forming a conducting channel even though at $V_G = 0$ V. Moreover, the decreased trap states would facilitate carrier transport, thus improved the mobility of TIPS-H$_2$BP.\textsuperscript{27}

On the other hand, the ribbon-shaped crystals of the metal complexes, TIPS-ZnBP and TIPS-CuBP, showed clearly lower hole mobilities compared with TIPS-H$_2$BP (Fig. 6b,c,e,f, and S4), although those values were much higher than the ones prepared by spin-coating method ($1.1 \times 10^{-5}$ cm$^2$V$^{-1}$s$^{-1}$ for TIPS-ZnBP and $5.6 \times 10^{-3}$ cm$^2$V$^{-1}$s$^{-1}$ for TIPS-CuBP).\textsuperscript{17} The maximum hole mobility of 0.12 cm$^2$V$^{-1}$s$^{-1}$ (average values of 0.05 cm$^2$V$^{-1}$s$^{-1}$ with 12 devices) with a threshold voltage $V_{th}$ of 6.6 V and on/off ratio $I_{on}/I_{off}$ of 7.6 x 10$^4$ for TIPS-ZnBP, while TIPS-CuBP showed the maximum hole mobility of 0.16 cm$^2$V$^{-1}$s$^{-1}$ (average values of 0.14 cm$^2$V$^{-1}$s$^{-1}$ with 4 devices) with a threshold voltage $V_{th}$ of 3.0 V and on/off ratio $I_{on}/I_{off}$ of 1.1 x 10$^5$. This result is rationalized by the fact that charge transport is suppressed in the cases of TIPS-ZnBP and TIPS-CuBP because of their triad-like structures (Fig. 3), clearly indicating the metalation had negative effects on the charge transport property.

Note that the I-V characteristics for TIPS-ZnBP device seem suppressed at high gate voltage, and the linear portion of the TIPS-H$_2$BP device shows current crowding. Although these reasons are not clear at this moment as the mechanisms are very complex, the carrier-density-dependent mobility and non-ideal behaviors.\textsuperscript{32} There are no conflicts to declare.

**Conflicts of interest**

**Acknowledgements**

This work was partly supported by CREST JST (No. JPMJCR15F1) and Grants-in-Aid for Scientific Research (Nos. JP20H02816, JP20H00379, JP20H05833, JP20H02711, JP20K15261). We thank Shohei Kato (NAIST) for XRD and X-ray single crystal analyses, and Sakiko Fujita and Tomoko Ohno (NAIST) for TEM measurement, respectively.

**Notes and references**
