Effect of molecular packing of zinc(II) porphyrins on the performance of field-effect transistors

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Abstract
The charge-transport phenomena of organic conjugated materials have been intensively investigated because of the potential applications of these materials in electronics and optoelectronics. Among these applications, organic field-effect transistors (OFETs) fabricated from either thin films or well-defined single crystals as charge-transporting layers are the most promising electronic devices. In this work, the effect of molecular packing on the performance of OFETs is investigated through the fabrication and characterization of devices based on zinc(II) porphyrins TPZ and TBPZ. The field-effect mobility of the transistors is found to increase with decreasing intermolecular distance, attributable to greater overlap of \( \pi \) orbitals among close-packed molecules and thereby enhance the charge transport.

Keywords: porphyrin, conjugated, organic field effect transistors, single crystal
Mathematics Subject Classification: 4.10, 5.12, 6.01

1. Introduction
Organic field-effect transistors (OFETs) are one of the most promising electronic devices when they are fabricated from either well-defined single crystals or well-ordered thin films as the charge-transporting layers [1, 2]. Charge carrier mobility in single crystals and thin films of organic conjugated materials has been investigated in attempts to improve electrical transport in organic semiconductors and thereby enhance the performance of organic electronic devices. Extensive research on electrical conduction in OFETs has revealed that the field-effect mobility is dependent not only on the fundamental properties of the molecules but also on factors such as grain size, interfacial modifications, and semiconductor thickness [3, 4]. The unique anisotropic arrangement of organic semiconductors owing to their strong intermolecular interactions is expected to have a considerable influence on the OFET performance because the larger overlap of \( \pi \)-orbitals between neighboring molecules may increase the bandwidth and facilitate charge transport [5–9]. However, the relationship between molecular packing and the mobility has not been confirmed yet due to the masking of such intrinsic conduction properties by the effects of structural defects and disorder at grain boundaries in thin films.

Porphyrin is an important complex molecule that offers a variety of optical, electrochemical, and catalytic properties. Because of their unique structure, porphyrins may provide multiple interactions such as hydrogen bonding, \( \pi-\pi \) stacking, electrostatic interactions, and metal–ligand coordination. However, in comparison with compounds such as acene, OFETs based on porphyrins have attracted little attention despite their being good candidates as electronic materials [10–13]. For a high degree of crystallinity with an excellent determinacy as well as a high corresponding device performance to be obtained, the extension of \( \pi \)-conjugation and the location of conjugative substituents on the porphyrin core may play a major role in terms of the molecular electronic energies and molecular arrangements during the formation of well-defined polycrystalline films or single crystals. Therefore, in this work, we fabricated and characterized field-effect transistors based on zinc(II) porphyrins TPZ and TBPZ. These molecules bearing different conjugated peripheral arms offer a variety of molecular packing and intermolecular distances within the crystal, which revealed a clear relationship...
between the molecular packing and the charge transport properties.

2. Experimental

2.1. Materials

Zinc(II) porphyrins TPZ and TBPZ were synthesized by following the known methods [14, 15]. TPZ consists of a zinc (II) porphyrin core and four 2-ethynyl-5-hexylthiophene peripheral arms while TBPZ consists of the same core and four 5-hexylthiophen-2-yl ethynyl phenyl arms (figure 1). These materials were found to have good film-forming properties and high solubilities in various solvents such as chloroform, dichloromethane, tetrahydrofuran, and chlorobenzene at room temperature.

Single crystals of TPZ and TBPZ were grown in air by carefully layering a 1 mM toluene solution of the respective compounds over methanol inside a glass tube (5–8 mm in diameter). The tube was then capped and allowed to reach equilibrium under darkness. Single crystals formed at the interface of the two solvents over a period of 3–7 d and were mounted for x-ray diffraction (XRD) data collection.

2.2. Instrumentation

Absorbance and emission spectra were obtained using an HP 8453 spectrophotometer (photodiode array type) and Hitachi F-7000 fluorescence spectrophotometer using quartz plates. All scanning electron microscopy (SEM) images were obtained using a Jeol JSM-7001F.

The XRD data for two porphyrins were collected on a Bruker SMART APEX diffractometer equipped with a monochromater in the MoKα (λ = 0.710 73 Å) incident beam. Each crystal was mounted on a glass fiber. The crystal data were integrated and scaled using the Bruker- SAINT software package, and the structure was solved and refined using SHEXTL V6.12. All hydrogen atoms were placed in the calculated positions.

2.3. OFET fabrication

Bottom gate top contact OFET devices consisted of heavily n-type doped (100) silicon as a gate electrode and 300 nm thick of thermally grown SiO2 as gate insulator. The source and drain electrodes (120 nm Au) were deposited by thermal evaporation through a shadow mask. The resulting wafers were washed with acetone, isopropanol, followed by ultraviolet–ozone exposure for further cleaning. The silicon oxide layer was treated with n-octyldichlorosilane (OTS) by immersing freshly cleaned wafers in a 8 mmol L⁻¹ solution of OTS in anhydrous toluene for 30 min, followed by sonication in toluene and isopropanol, consecutively. The thin-film transistors were fabricated by directly spin-coating a 1% solution of porphyrins onto the dielectric substrate at 1600 rpm. The single-crystal OFET devices were fabricated by growing of porphyrin crystals directly on the top of OTS-treated SiO2 insulator by dissolving TPZ and TBPZ in toluene and slow diffusion over n-hexane to grow high quality crystalline needles. The source and drain electrodes were then thermally evaporated (120 nm in thickness). All field-effect mobilities were extracted in the saturation regime. The device performance was evaluated in air using 4200-SCS semiconductor characterization system in ambient conditions. For the light source, a xenon lamp (Thermo Oriel) equipped with an optical fiber and high-speed monochromator (Oriel Cornerstone™ 130 1/8 m monochromator) were employed. The light illumination power was measured by using a Newport 2385-C Si photodetector with a calibration module.

3. Results and discussion

3.1. Crystal structures and crystal packing diagrams

SEM analysis revealed these crystalline objects to be collections of fairly uniform needles with very high aspect ratios for both TPZ and TBPZ; the widths ranged from several micrometers to tens of micrometers (figures 2(d) and (f)).
The single-crystal x-ray crystallographic structures of TPZ and TBPZ are shown in figure 2. As expected, the porphyrin cores in TPZ are nearly planar while the porphyrin core in TBPZ is puckered with angles between N1/N2/N3/N4 plane and each pyrrol ring of 6.8°, 13.3°, 9.1°, and 10.8°. For TPZ, three thiophene rings are a little tilted with respect to the N1/N2/N3/N4 porphyrin core plane in the range of 7.0(2)°–12.2(2)° and the fourth tethered thiophene rings are tilted significantly from the porphyrin plane by 22.8(2)°. For TBPZ, four phenyl rings are tilted from the N1/N2/N3/N4 porphyrin core plane by 47.3°, 77.7°, 48.1°, and 80.4°. Four thiophene rings are also tilted with respect to the porphyrin core plane by 27.7°, 30.4°, 34.4°, and 49.9°. In the packing diagram representations of TPZ, two molecules act remarkably as a dimeric pair of porphyrins with a closest atom–atom distance of 3.06(3) Å (figure 2(c)). These porphyrin pairs are stacked in a dramatic staircase fashion through π–π interactions, with closest atom–atom distances of 3.34(3) Å. The H-aggregated dimeric pairs were aligned in a J-aggregation manner, which is capable of facilitating intermolecular carrier hopping and has slip-stacked carrier transport properties. In the packing diagram representations of TBPZ, porphyrins are adopting multi-layered arrangements (figure 2(e)) generating an array with maximizing their van der Waals interactions. The
The second layer is stacked slightly slipped-manner to the first layer, and each layer is piled up in a zigzag fashion. The distance between layers is found to be 3.65 Å, longer than that of TPZ.

The lattice parameters determined for TPZ single crystal are $C_{68}H_{68}N_4S_4Zn$, $MW = 1134.87$, triclinic $(P-1)$, $a = 12.53$ (3) Å, $b = 15.49(3)$ Å, $c = 16.70(3)$ Å, $\alpha = 72.16(3)^\circ$, $\beta = 86.59(3)^\circ$, $\gamma = 68.50(3)^\circ$, $V = 2866.1(10)$ Å$^3$. 

### Figure 4
Output (a) and transfer curves (b) of organic thin film transistors made of TPZ and TBPZ.

### Figure 5
Output (a) and transfer curves (b) of single crystal OFET devices made of TPZ and TBPZ; optical microscopy images of FET devices of TPZ (c) and TBPZ (d).

### Table 1
Crystallographic parameters and field-effect mobility of TPZ and TBPZ. $D$ indicates intermolecular distance among neighboring layers.

| Sample | $a$(Å) | $b$(Å) | $c$(Å) | $V$(Å$^3$) | $D$(Å) | $\mu_{max}$(cm$^2$ V$^{-1}$ s$^{-1}$) | $I_{on/off}$ | $L_{on/off}$ |
|--------|--------|--------|--------|-----------|--------|-------------------------------|-------------|------------|
|        | Film   | Crystal| Film   | Crystal   |        |                               |             |            |
| TPZ    | 12.53  | 15.49  | 16.70  | 2866.1    | 3.34   | 1.2                           | $1.5 \times 10^8$ | $10^3$     |
| TBPZ   | 8.75   | 20.04  | 21.69  | 3743.4    | 3.65   | $2.3 \times 10^{-4}$          | $0.32$      | $5 \times 10^3$ | $10^3$     |

The lattice parameters determined for TPZ single crystal are $C_{68}H_{68}N_4S_4Zn$, $MW = 1134.87$, triclinic $(P-1)$, $a = 12.53$ (3) Å, $b = 15.49(3)$ Å, $c = 16.70(3)$ Å, $\alpha = 72.16(3)^\circ$, $\beta = 86.59 (3)^\circ$, $\gamma = 68.50(3)^\circ$, $V = 2866.1(10)$ Å$^3$. 

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The lattice parameters determined for TBPZ single crystal are $C_{97}H_{84}N_{4}S_{4}Zn$, MW = 1439.24, triclinic, $a = 8.75(17)$ Å, $b = 20.04(4)$ Å, $c = 21.69(4)$ Å, $\alpha = 82.706(4)^\circ$, $\beta = 85.123(4)^\circ$, $\gamma = 84.063(4)^\circ$, $V = 3743.4(13)$ Å$^3$.

3.2. Optical properties

The UV–vis absorption spectra in solution and film forms of TPZ and TBPZ show that TPZ generates densely packed aggregates in the solid state (figure 3). The solution samples were prepared in chloroform with a concentration of $1 \times 10^{-6}$ M, and the thin-film samples were fabricated by spin-coating the chloroform solutions of these molecules.

The solution sample of TBPZ exhibits Soret-bands at 427 nm with multiple Q-bands around 553 nm, the extinction spectrum of film from TBPZ on quartz glass plates shows a broadened and slightly red-shifted Soret-band at 435 nm and red-shifted multiple Q-bands around 561 nm. However, in the case of TPZ, a drastic spectral change was observed in the film states, which is attributed to the high degree of intermolecular interaction between the porphyrins. In particular, the absorption spectrum is significantly broadened and red-shifted, which is unequivocal evidence of the mixed formation of H-aggregated dimers and the J-aggregated set of molecules with the closest limited distances, supporting the above single-crystal results.

3.3. OFET performance

To investigate the charge-transport properties of TPZ and TBPZ, OFETs (bottom-gate, top-contact) were fabricated on OTS–SiO$_2$/Si substrates, with n-doped polycrystalline silicon as the gate electrode, an OTS-treated SiO$_2$ surface layer as the dielectric gate insulator, and gold electrodes deposited using shadow masks. The film devices were prepared by spin-coating the chloroform solutions of the porphyrins, and the needle-crystal devices were prepared via the slow diffusion of toluene solutions over n-hexane. The devices were dried under vacuum at room temperature for 24 h before testing at room temperature in air.

These OFET devices show typical p-channel FET characteristics as shown in figures 5. The output characteristics show very good saturation behaviors and clear saturation currents that are quadratically related to the gate bias, even using Au based source/drain electrodes with a relatively large electron injection barrier (figures 4(a) and 5(a)).

The carrier mobility ($\mu$) was calculated by using the saturation region transistor equation

$$I_{DS} = \frac{W}{2L} \mu C_0 (V_G - V_T)^2,$$

Figure 6. Transfer characteristics of OFET devices; transfer curves of thin film devices ((a) and (b)) and single crystal devices ((c) and (d)) made of TPZ and TBPZ, respectively, in the dark and under monochromatic light irradiation ($I = 5.6 \mu W cm^{-2}$).
respectively. According to the transfer characteristics of the crystal OFETs of TPZ and TBPZ, where the channel mobility of TPZ and TBPZ provided field-effect mobilities of 1.2 and 2.3 × 10⁻⁴ cm² V⁻¹ s⁻¹, respectively, together with high on/off current ratios (I_on/off = 1.5 × 10⁶ and 5 × 10⁷, respectively).

The crystalline-needle OFETs made of TPZ and TBPZ provided field-effect mobilities of 3.1 and 0.32 cm² V⁻¹ s⁻¹, respectively, together with high on/off current ratio of >10⁷. The mobility of the TBPZ single-crystal devices was 1400 times higher than that of the film-state ones, while the mobility of TPZ single-crystal devices was 2.5 times higher than that of the film-state devices. The dramatic increase in the mobility of the TBPZ single-crystal devices is presumably due to the denser molecular confinement, while the slight increase in mobility for the TPZ single-crystal devices indicates that a highly and densely packed arrangement of polycrystallites has already been achieved in the solid film state (figure 5(b)). Remarkably, the mobility dramatically increases with decreasing intermolecular distance (table 1). Thus, closer packing of molecules, which increases the overlap of π orbital, is expected to result in higher conduction and, thus, higher field-effect mobility.

Furthermore, OFETs made of TPZ and TBPZ displayed photoinduced enhancement of the source–drain current (I_DS). Organic phototransistor (OPT) devices of TPZ and TBPZ (figure 6) showed a clear increase in I_DS when illuminated with incident light. It should be emphasized that the clearly increase in I_DS was induced by the illumination of light extremely low intensity (5.6 μW cm⁻²). This large increment in drain current was ascribed to (i) the trapping of photo-generated charge carriers in the organic layer, leading to the injection and accumulation of additional holes in the active layer, and (ii) the screening of the gate voltage by a built-in field resulting from the charges trapped at the interface with the dielectric gate insulator [17].

4. Conclusion

High-performance OFET devices from both thin films and single-crystalline needles were fabricated using highly soluble porphyrins TPZ and TBPZ. The high performance of the TPZ-based OFET is mainly due to the very intriguing J-aggregation of H-aggregated dimeric porphyrin pairs in the crystalline structures, resulting in stronger intermolecular π–π interactions incorporating unusually short layer distances, which enhance the charge-transport efficiency. It was revealed that the mobility of OFETs increases with decreasing intermolecular distance in the organic crystal. The enhancement of the mobility can be attributed to increased π overlap among neighboring molecules and consequent promotion of the charge transport. This result indicates that the extension of conjugated peripheral arms play an important role in the design of new porphyrin derivatives for the field-effect transistors.

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