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High-Performance Single-Crystal-Based Organic Field-Effect Transistors from π-Extended Porphyrin Derivatives

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Significant research interests have recently emerged for the development of new materials for organic field-effect transistors (OFETs), due to their great promise for use in electronic and optoelectronic applications.^[1,2] Among them, porphyrin derivatives are of particular interest because of their unique properties in photonic and electronics.^[3] As a large and flat conjugated tetrapyrrole macrocycle that can be decorated with a variety of metals and substituents, porphyrins have been widely used in solar energy conversion, electron transfer, and artificial photosynthesis,^[4] but they have been relatively less exploited as building blocks for the fabrication of OFETs.^[5]

In fact, most of the organic semiconductors rely on the inherent structural uniqueness of building blocks, such as planarity and π conjugation, and their packing and interactions with adjoining building blocks. In this regard, porphyrins would be one of the best candidates for organic transistors because they could impart multiple inter- and/or intra-interactions, such as hydrogen bonding, π - π stacking, electrostatic interactions, as well as metal-ligand coordination that could be generated by synthetic modification of the porphyrin framework.^[6] Therefore, well-defined crystalline nano- and micro-size structures, such as fibers, rods, ribbons, plates, sheets, cubes, wheels, rings, and grids, are successfully reported.^[3,7]

However, the performance of OFET devices based on porphyrin derivatives show relatively low carrier mobility, with a range of 10^{-6} to 10^{-1} cm²V⁻¹s⁻¹, compared with their inorganic analogues,^[5] although they have great potentials as mentioned above. Most of the porphyrin OFET devices are based on thin films or crystalline objects prepared by spincoating or vacuum-deposition processes. Therefore, a deeper interpretation of systems has hardly succeeded due to the lack of information about the molecular structure and pack-

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ing of building blocks at the molecular level that are closely related with the performance of OFET.^[1,2] Most of high performance non-porphyrin organic semiconductors are based on highly ordered molecular packing with strong π - π interactions, showing high crystallinity. However, structural studies of these organic semiconductors have also rarely been exploited due to the difficulties of single-crystal growth even with small conjugated molecules, such as pentacene, rubrene, and anthracene derivatives. Nevertheless, recent achievement on porphyrin-based crystalline OFETs has been successfully demonstrated, but showed relatively low device performance.^[8]

Herein, we report on single crystalline wires from π -extended porphyrin derivatives **TTPH2** and **TTPZn**, and their unique electronic properties in OFET devices along with single-crystal structures.

TTPH2 was readily obtained in relatively high yield (21%) by using a typical porphyrin condensation reaction between 4-((5-hexylthiophene-2-yl)ethynyl)benzaldehyde and pyrrole in propionic acid. **TTPZn** was further obtained by metallation of **TTPH2** with $Zn(OAc)_2$ in 78% yield (Scheme 1). Detailed synthetic procedures are described in the Supporting Information section (Scheme S1). Cyclic voltammetry analysis of **TTPH2** and **TTPZn** reveals that HOMO, LUMO, and bandgap energy (E_g) are found to be -5.33, -3.40, and 1.93 eV for **TTPH2** and -5.28, -3.48, and 1.80 eV for **TTPZn**, respectively (Table S1). A relatively low bandgap is found in metalloporphyrin **TTPZn**.

Upon layering solutions of **TTPH2** and **TTPZn** in toluene over hexanes and allowing the resulting mixtures to stand over 7–14 days, narrowly dispersed single-crystalline wires were obtained in both cases, which were around $300-500 \,\mu\text{m}$ in length and about 4–15 μm in width identified by scanning electron microscopy (SEM) analysis (Figure 1).

The single-crystal X-ray structures of **TTPH2** and **TTPZn** are shown in Figure 2. The porphyrin core in **TTPH2** is puckered with angles between the N1/N2/N3/N4 plane and each pyrrol ring of 10.8° (N1/C2/C3/C4/C5), 7.2° (N2/C7/C8/C9/C10), 11.6° (N3/C12/C13/C14/C15), and 7.6° (N4/C17/C18/C19/C20) as shown in Figure 2 a and b and Figure S1 in the Supporting Information. Interestingly, the porphyrin core in **TTPZn** is also puckered with angles between the N1/N2/N3/N4 plane and each pyrrol ring of 6.8, 13.3, 9.1, and 10.8° (Figure 2 f and g and Figure S3 in the Supporting Information). Four phenyl rings are tilted from the N1/N2/



Scheme 1. Porphyrin building blocks.



Figure 1. SEM (a and b) and optical microscopy (c and d) images of single-crystalline wires obtained from **TTPH2** (a and c) and **TTPZn** (b and d).

N3/N4 porphyrin core plane by 52.7, 79.3, 53.7, and 80.8° for **TTPH2**, and by 47.3, 77.7, 48.1, and 80.4° for **TTPZn**. Four thiophene rings are also tilted with respect to the porphyrin core plane by 20.4, 25.7, 32.8, and 43.3° for **TTPH2**,

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and 27.7, 30.4, 34.4, and 49.9° for **TTPZn**. Great similarities are found in the crystal structures and crystal packing in both systems. In the packing diagram representations, the porphyrins adopt multi-layered arrangements (Figure 2c and h) generating an array, which maximizes their van der Waals interactions (Figures S2 and S4 in the Supporting Information). The second layer is stacked in a slightly slipped manner with respect to the first layer, and each layer is piled up in a zig-zag fashion (ababa type) in both **TTPH2** and **TTPZn** crystals (Figure 2e and j). However, the distances between the layers are quite different and are found to be 3.81 Å for **TTPH2** and 3.65 Å for **TTPZn**.

To investigate the electrical characteristics of individual single crystals of **TTPH2** and **TTPZn**, OFETs (bottom-gate, top-contact) were fabricated on a SiO₂/Si substrate with N-doped polycrystalline silicon as a gate electrode and an *n*-octyltrichlorosilane (OTS)-treated SiO₂ surface layer as a dielectric gate insulator followed by deposition of gold electrodes using shadow masks. The channel lengths are 110 μ m for **TTPH2** and 103 μ m for **TTPZn**. The devices were dried in vacuum at room temperature for 24 h before testing them at room temperature and in air.

The resulting single-crystal OFET devices show typical pchannel FET characteristics as shown in Figure 3. The output characteristics show very good saturation behavior 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.^[9]

The carrier mobility (μ) was calculated by using the saturation region transistor equation, $I_{\rm DS} = (W/2L)\mu C_0 (V_G - V_t)^2$, in which I_{DS} is the source-drain current, V_{G} the gate voltage, C_0 the capacitance per unit area of the dielectric layer, and $V_{\rm t}$ the threshold voltage.^[10] Experimental results indicate that the devices fabricated from single crystal of TTPH2 and TTPZn display excellent OFET performances. The carrier mobilities are $6.2 \times 10^{-2} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ for **TTPH2** and $0.32\ \text{cm}^2 V^{-1} \text{s}^{-1} \text{for } \textbf{TTPZn}$ with a high on–off current ratio of $>10^4$ (Figure 3). To the best of our knowledge, these values are among the best for porphyrin-based OFET devices.^[5] Since the mobility is highly dependent on the stacking distance between building blocks in the solid state, the single-crystal device of TTPZn, which has the shorter packing distance between layers, shows much better device performance than that of TTPH2 evidenced by single-crystal X-ray structure analysis. The smaller bandgap (E_g) of **TTPZn** ($E_g = 1.80 \text{ eV}$) compared with **TTPH2** ($E_g = 1.93 \text{ eV}$) further supports that the Zn metallation could make the porphyrin system behave as a better FET device.

For comparison, we have also investigated the performances of the corresponding film devices prepared by spin coating the solutions of **TTPH2** and **TTPZn** in chloroform. Interestingly, the device performances drop down dramatically and the observed carrier mobilities (μ) are in the range of about 2.3×10^{-4} - 3.5×10^{-4} cm²V⁻¹s⁻¹ (Figure S7 and S8 in the Supporting Information). These dramatic drops in mobility are presumably due to a decrease of their molecular order upon haphazard aggregations of porphyrins during the

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Figure 2. Single-crystal X-ray structures and packing diagram representations of **TTPH2** (a–e) and **TTPZn** (f–i). Hydrogen atoms are omitted for clarity.

film formation. However, the UV/Vis absorption and photoluminescence (PL) spectra in solution and film forms of **TTPH2** and **TTPZn** show that **TTPZn** generates densely packed aggregates in the solid state (Figure S6 in the Supporting Information). The absorption spectra reveal slight redshifts of around 5–8 nm upon the film formation in both **TTPH2** and **TTPZn** that indicate ineffective intermolecular interactions. For example, the solution sample of **TTPH2** exhibits Sorét bands at 426 nm with multiple Q bands around 474 nm, the extinction spectrum of the film from **TTPH2** on quartz glass plates shows a broadened and slightly redshifted Sorét band at 433 nm and redshifted multiple Q bands around 522 nm. The PL spectrum of the film from **TTPH2** However, carrier mobilities for both film systems of **TTPH2** and **TTPZn** show similar values that are much lower compared with their crystal analogues. Although **TTPZn** is providing heavily packed aggregation and low bandgap, lack of molecular order in the film is responsible for low mobility, which is similar to that of the **TTPH2** film.

In summary, single crystals of new porphyrin derivatives **TTPH2** and **TTPZn** have been obtained from slow diffusion of solvents. The OFET devices based on these single crystals display excellent characteristics with high mobilities of $6.2 \times 10^{-2} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ for **TTPH2** and $0.32 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ for **TTPZn** with a high on–off current ratio of $> 10^4$. Due to low crystal-linity, their film device performances drop dramatically.

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720 nm, whereas two bands at 664 and 724 nm are observed for the solution sample of TTPH2 (Figure S6a in the Supporting Information). Therefore, insignificant configurational changes are observed upon film formation. However, in case of TTPZn, the extinction spectrum of the film shows a broadened and slightly redshifted Sorét band at 432 nm and redshifted multiple Q bands around 557 nm. The PL spectrum of the film from TTPZn shows one broad band at 646 nm showing the typical behavior of a closely aggregated system, whereas two bands at 602 and 647 nm are observed for the solution sample of TTPZn (Figure S6b in the Supporting Information). This observation suggests that TTPZn is becoming much more tightly packed upon film formation and therefore better crystal

shows two bands at 658 and

device performance is expected. Differential scanning calorimetric (DSC) measurements further assist the densely packed aggregation of the TTPZn film. They exhibit distinct crystalline-isotropic transition temperatures of 263 and 321 °C for TTPH2 and TTPZn films, respectively (Figure S9 in the Supporting Information). A relatively high melting temperature is observed for the TTPZn film that is strongly related to the high density of tightly packed metalloporphyrins.

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Figure 3. Electrical characterization of single-crystal OFETs. Output (a) and transfer (b) curves of OFET device made of **TTPH2** (Inset: SEM image of device, $V_{DS} = -80$ V), and output (c) and transfer (d) curves of OFET device made of **TTPZn** (Inset: SEM image of device, $V_{DS} = -110$ V).

These new porphyrin derivatives have demonstrated that porphyrin building blocks have strong potential for use in electronic and optoelectronic applications.

Experimental Section

Crystal data for **TTPH2**: CCDC-811952; $C_{92}H_{86}N_4S_4$; MW = 1375.89; Triclinic; a=9.1290(18), b=20.121(4), c=21.611(4) Å; a=86.12(3), $\beta=82.87(3)$, $\gamma=87.06(3)^\circ$; V=3926.2(13) Å³; Z=2; $\mu(Mo_{Ka})=0.169$ mm⁻¹; 22008 reflections measured; 15074 unique ($R_{iat}=0.1000$), which were used in all calculations; final R=0.0875 (Rw=0.1875) with reflections having intensities greater than 2σ ; GOF (F^2)=0.847. Crystal data for **TTPZn**: CCDC-811953; $C_{92}H_{84}N_4S_4Zn$; MW=1439.24; Triclinic; a=8.7528(17), b=20.041(4), c=21.689(4) Å; a=82.706(4), $\beta=85.123(4)$, $\gamma=84.063(4)^\circ$; V=3743.4(13) Å³; Z=2; $\mu(Mo_{Ka})=0.490$ mm⁻¹; 21101 reflections measured; 14361 unique ($R_{iat}=0.0976$), which were used in all calculations, final R=0.0508 (Rw=0.0961) with reflections having intensities greater than 2σ ; GOF (F^2)=0.583. The supplementary crystallographic data for this paper can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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