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### COMMUNICATION

# Organic semiconductors based on annelated $\beta$ -oligothiophenes and its application for organic field-effect transistors<sup>†</sup>

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Organic field-effect transistors based on two derivatives of annelated  $\beta$ -oligothiophenes are fabricated. High mobility of 2.2 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> is obtained for 2,5-distyryl-dithieno[2,3-*b*:3',2'-*d*]thiophene (DEP-DTT) while 2,5-diphenyl-dithieno[2,3-*b*:3',2'-*d*]thiophene (DP-DTT) presents no field-effect characteristics. The existence of S- $\pi$  intermolecular interaction in DEP-DTT, which is introduced by C=C double bonds, plays an important role in the molecular arrangement both in single crystal and thin film structures, and the charge transport of organic field-effect transistors.

Organic electronics have attracted particular attention due to their potential advantages of flexibility, large-area process, and lightweight.1 As an important kind of organic electronics, organic fieldeffect transistors (OFETs) have earned significant progress in the past few decades.<sup>2</sup> Some OFETs based on small organic molecules exhibit better performance than their inorganic counterparts (conventional α-H: silicon-based transistors).<sup>3,4</sup> Usually, these small organic molecules with high field-effect mobilities were synthesized by enhancing the degree of extended  $\pi$ -conjugation, which is expected to provide more efficient  $\pi$  orbital overlap and lead to high field-effect mobility. Normally, organic semiconductors are coalesced with weak intermolecular interactions, such as Van der Waals,  $\pi$ - $\pi$ , and C-H interactions. On the contrary, it is known that the inorganic semiconductors are combined with strong covalent bonds and possess high mobility even in amorphous structure. For organic semiconductors, strengthening intermolecular interactions may be a possible way to improve the mobility.1b However, detailed studies in this domain are rarely investigated. It is still a significant challenge to understand the relationship between the intermolecular interaction and the device performance.

Recently, a high field-effect mobility of 2.0 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> was obtained in annelated  $\beta$ -oligothiophenes derivatives.<sup>5a</sup> It is very interesting that the multiple S–S close contacts in annelated

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 $\beta$ -oligothiophenes derivatives make the molecules adopt a compressed herringbone arrangement and provide another charge transport pathway.<sup>5</sup> In our previous work,<sup>6</sup> we found that there exists several kinds of intermolecular interactions, such as C–S, S–S,  $\pi$ – $\pi$ and S- $\pi$  interactions, in the helicenes based on annelated  $\beta$ -oligothiophenes.<sup>7</sup> In the presence of *n*-BuLi, the ring opening occurs at the position of the middle S atom in derivatives of dithieno [2,3-b:3',2'-d]thiophene (DTT),8a which implies the middle S atom is more electropositive than the other two S atoms. It is likely to generate the intermolecular interaction between the electropositive S atom and the other atoms on the neighboring DTT unit. In this paper, we synthesized two annelated β-oligothiophenes: 2,5-diphenyl-dithieno [2,3-b:3',2'-d]thiophene (DP-DTT) and 2,5-distyryl-dithieno [2,3-b:3',2'-d]thiophene (DEP-DTT). A high mobility of 2.2 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> was obtained for DEP-DTT, which was attributed to the formation of S- $\pi$  intermolecular interactions.

The molecular structures of DP-DTT and DEP-DTT are shown in Fig. 1(a) and (b). DP-DTT was synthesized according to our previous work,<sup>8</sup> starting from DTT. The compound of DEP-DTT was prepared from dithieno[2,3-*b*:3',2'-*d*]thiophene-2,5-dicarbox-aldehyde<sup>8</sup> through Wittig reaction with benzyl chloride. All compounds were purified three times by thermal gradient sublimation prior to processing. All these materials have thermal stability with a decomposition temperature of 307 °C for DP-DTT and 330 °C for DEP-DTT (supporting information<sup>†</sup>), respectively. OFETs based on these two compounds were fabricated with top contact geometry. It is surprising that a high field-effect mobility of



Fig. 1 The molecular structures of DP-DTT (a) and DEP-DTT (b). Output (c) and transfer (d) curves of OFETs based on DEP-DTT at substrate temperature of 70  $^{\circ}$ C.

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2.2 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> is obtained in the devices with DEP-DTT as the active layer, while the devices based on DP-DTT present no field-effect characteristics. The output and transfer curves of OFETs based on DEP-DTT with a substrate temperature ( $T_S$ ) of 70 °C are shown in Fig. 1(c) and (d). The output and transfer curves possess typical p-type characteristics. Unfortunately, the devices present a high threshold voltage ( $V_T$ ) and a low contact resistance in spite of the HOMO value at 4.80 eV. Table 1 lists the characteristics of OFETs with DEP-DTT as the active layer at different  $T_S$ . There is no dramatic change of device mobility after three months in the natural environment.

In order to further understand the tremendous difference between the properties of OFETs based on DP-DTT and DEP-DTT, the topographical images of these compounds films were investigated by atomic force microscope (AFM). Fig. 2 shows the topographical images of DP-DTT (Fig. 2a-b) and DEP-DTT (Fig. 2c-e) films at different  $T_{\rm S}$ . As shown in Fig. 2(a) and (b), the films of DP-DTT are homogeneous and amorphous. For DEP-DTT, the topographical images present a lamellar structure even when the  $T_{\rm S}$  is room temperature (RT). For these three images of DEP-DTT films at different  $T_{\rm S}$ , the average layer spacing is around 2.0 nm. On the other hand, a series of progressional peaks (001) are observed in the X-ray diffraction patterns of DEP-DTT as shown in Fig. 2(f). This indicates the films of DEP-DTT are highly crystalline. The d-spacing calculated according to Bragg's equation is about 2.0 nm, which is consistent with that obtained from AFM. But for DP-DTT, the X-ray diffraction patterns indicate that the films of DP-DTT are amorphous.

As we know, the difference between the molecular structures of DP-DTT and DEP-DTT is the C=C double bond. So it becomes necessary to further investigate the effect of introducing C=C double bonds into the molecular structures. Fig. 3 shows the single crystal structures and the intermolecular interactions of DP-DTT and DEP-DTT. For DP-DTT, the molecular long axis is the c axis with a length of 12.7 Å. The terminal phenyl groups contort from the plane of the DTT unit, as shown in Fig. 3(a). The twisted angles are about 14.2° and 18.8°, respectively. Due to these large twisted angles, it may be implied that the extended  $\pi$  orbit is partially formed between the phenyl groups and the DTT unit. As shown in Fig. 3(b), the distance between the middle S atoms of two neighboring DTT units is 3.560 Å, which is smaller than the sum of the S atoms' Van der Waals radius (3.70 Å). This short contact is normally considered as an intermolecular interaction. In addition, the DP-DTT molecules adopt a herringbone arrangement with a  $\pi$ - $\pi$ spacing of 3.578 Å. The herringbone angle is about 79.3°. However, the S-S intermolecular interaction is not observed among the molecules at the neighboring rows marked with the dot-dashed line in Fig. 3(c). In DEP-DTT, the terminal phenyl groups almost lie on

**Table 1** The characteristics of OFETs based on DEP-DTT at differentsubstrate temperature  $(T_S)$ 

Compound	$T_{\rm S}$ (°C)	$\mu \ (\mathrm{cm}^2 \ \mathrm{V}^{-1} \ \mathrm{s}^{-1})^a$	$V_{\mathrm{T}}(\mathrm{V})^{a}$	$I_{\rm on}/I_{\rm off}$
DEP-DTT	RT	1.2-2.0	-65  to  -68	105
	100	0.6–1.5	-58  to  -68 -64  to  -69	10 <sup>5</sup>

<sup>*a*</sup> All data were extracted from more than ten devices.



Fig. 2 Topographical images and X-ray diffraction patterns at different substrate temperature: (a) RT of DP-DTT; (b) 70 °C of DP-DTT; (c) RT of DEP-DTT; (d) 70 °C of DEP-DTT; (e) 100 °C of DEP-DTT; (f) X-ray diffraction patterns. The areas of the topographical images are all 4  $\mu$ m × 4  $\mu$ m.



**Fig. 3** Single crystal structures and intermolecular interactions in the single crystals of DP-DTT (left column) and DEP-DTT (right column): (a) and (d) side-view; (b) and (e) intermolecular interaction; (c) and (f) crystal packing. The dashed line presents the close contact between atoms. The dot-dashed line indicates the molecular situation in one row.

the plane of the DTT unit with smaller dihedral angles of 2.9° and 4.3°. As a consequence, the DEP-DTT molecule presents a bowed shape, as shown in Fig. 3(d). Furthermore, it is unexpected that the S-S intermolecular interaction disappears with the emergence of multiple S-C intermolecular interactions in DEP-DTT, as shown in Fig. 3(e). The distances between C atoms and the middle S atom of the neighboring DTT unit are 3.422 Å, 3.378 Å, 3.481 Å, and 3.417 Å, respectively. As discussed above, the middle S atom of the DTT unit is more electropositive, which causes the formation of these multiple S-C intermolecular interaction. Due to the coplanar structure of the styryl groups and the DTT unit, the extended  $\pi$ orbit is formed and these multiple S-C intermolecular interactions convert into S- $\pi$  intermolecular interactions. At the same time, DEP-DTT molecules also adopt a herringbone arrangement with a  $\pi$ - $\pi$  spacing of 2.575 A. The herringbone angle is about 52.0°, which is smaller than that of sexithiophene (66°) and nearly equal to that of pentacene (53°).<sup>9</sup> Compared with that of DP-DTT, it can be concluded that DEP-DTT molecules adopt a condensed packing. It is evident that the introduction of a C=C double bond into DEP-DTT causes the formation of S- $\pi$  intermolecular interaction and results in a condensed molecular packing. Furthermore, the molecular long axis is also the c axis with a length of 20.8 Å, which is consistent with the layer spacing (2.0 nm) obtained from AFM and the *d*-spacing (2.0 nm) obtained from X-ray diffraction patterns. This demonstrates that DEP-DTT molecules maintain a consistent structure in the film and single crystal. Furthermore, the formation of S- $\pi$  intermolecular interaction not only causes the molecular arrangement to adopt a condensed packing in the single crystal and film structures, as discussed above, but also benefits the charge transport. The netlike S- $\pi$  intermolecular interaction may act as a spring bed to enhance the hopping ability or diversify the transport of charges, as illustrated in Fig. 4. So DEP-DTT possesses a high field-effect mobility.

In conclusion, two  $\beta$ -oligothiophenes derivates: DP-DTT and DEP-DTT were synthesized. A high field-effect mobility of 2.2 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> was obtained in DEP-DTT while DP-DTT presents

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assisted by the S- $\pi$  intermolecular interaction.

no field-effect characteristics. The introduction of a C=C double bond causes the formation of S- $\pi$  intermolecular interaction in DEP-DTT, which plays an important role in the molecular arrangement in single crystal and film structures, and has a significant contribution to charge transport in OFETs. It will help us to design and synthesize new organic semiconductors with high field-effect mobility by utilizing the various intermolecular interactions.

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transport. The line with an arrow presents the charge transport under

field-effect. The dashed line with an arrow illustrates the charge transport