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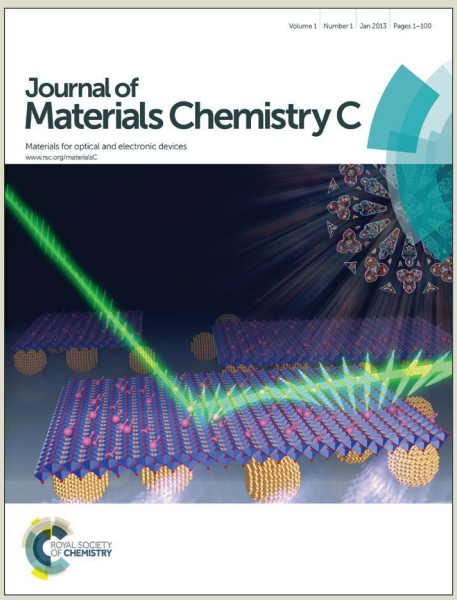

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Isomers of organic semiconductors based on dithienothiophenes: the effect of sulphur atoms positions on the intermolecular interactions and field-effect performances†

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2,5-distyryl-dithieno[2,3-*b*:2',3'-*d*]thiophene (**DEP-*bt*-DTT**), an isomer of 2,5-distyryl-dithieno [2,3-*b*:3',2'-*d*]thiophene (**DEP-*bb*-DTT**) and 2,5-distyryl-dithieno[3,2-*b*:2',3'-*d*]thiophene (**DEP-*tt*-DTT**), was synthesized. Organic field-effect transistors (OFETs) based on these three isomers were fabricated. The structural parameters and the formation of the intermelcular interactions in their single crystals show regular change when the positions of sulphur atoms vary from *top-bottom-top* in **DEP-*tt*-DTT** to *bottom-bottom-top* in **DEP-*bt*-DTT**, then to *bottom-bottom-bottom* in **DEP-*bb*-DTT**. Combining with the results of theoretical calculations and OFETs performances, it reveals that: 1) the poistions of sulphur atoms determine the contribution extent of sulphur atoms to the molecular conjugation and the formation of the intermolecular interactions; 2) the existing of the intermolecular interactions, especially for S–π, benefits for the charge transport; 3) the field-effect mobility (μ) increase with the increasing of the sulphur atoms contribution to the molecular conjugation.

Introduction

Over the past decades, organic electronics have received more attentions due to their potential advantages of flexibility, light-weight, large-area process and low cost.[1-10] Organic field-effect transistors (OFETs) are one of the important components of modern organic electronics. Their performances have been improved by adopting new organic semiconductors or optimizing the devices configuration.[6-28] Based on these efforts, the field-effect mobilities (μ) of OFETs have reached and even exceeded their inorganic counterparts (conventional α-H: silicon-based transistors), especially for OFETs with small molecules as active layers.[29-34] However, they are still lower than that of inorganic devices based on polysilicon and monocrystalline silicon. The major difference between inorganic and organic semiconductors is the combination mode. For organic semiconductors, they are coalesced via weak intermolecular interactions, such as Van der Waals interaction, S–S interaction, π–π interaction, and C–H interaction, instead of strong covalence bonds in inorganic semiconductors.[35-39] So it may be an effective way to improve the performance of OFETs by enhancing intermolecular interactions.

Dithienothiophene (**DTT**) derivatives, as analogues of acenes, have shown considerable mobility.[35-48] For these fused thiophene structures, there may form various intermolecular interactions including weak hydrogen bonding, π–π stacking, C–H interactions, and S–S interactions. In our previous works, it was found that the introduction of C=C double bond can cause the formation of S–π intermolecular interaction and is responsible for the high μ of 2.2 cm^2/Vs in 2,5-distyryl-dithieno[2,3-*b*:3',2'-*d*]thiophene (**DEP-*bb*-DTT**).[38] Furthermore, the intermolecular interactions can transform from S–S in 2,5-diphenyl-dithieno[2,3-*b*:3',2'-*d*]thiophene (**DP-*bb*-DTT**) with no field effect, to S–C in 2,5-dibiphenyl-dithieno[2,3-*b*:3',2'-*d*]thiophene (**DBP-*bb*-DTT**) with μ of 0.45 cm^2/Vs, to S–π in **DEP-*bb*-DTT**, and to the coexisting of S–S and S–π in 1,4-di[2-dithieno[2,3-*b*:3',2'-*d*]thiophen-2-yl-vinyl]-benzene (**D-*bb*-DTT-EP**) with μ of 0.15 cm^2/Vs as the end-capping groups changing. Combining the theoretical calculations, it can be concluded that the intermolecular interactions act as an important role in the devices performances.[39] But for 2,5-distyryl-dithieno[3,2-*b*:2',3'-*d*]thiophene (**DEP-*tt*-DTT**), there also exists S–S and S–C intermolecular interactions in the single crystal while μ of 0.17 cm^2/Vs was obtained from OFETs.[37] It was obvious that the difference of sulphur atoms positions between the isomers of **DEP-*bb*-DTT** and **DEP-*tt*-DTT** causes a dramatic change in the devices performances. In this field, there has no report about the relationship between the devices performances and the isomers of organic semiconductors, except the studies on the isomerization and substituting position of alkyl chains.[49] As we all know, the isomers are different organic molecules that have

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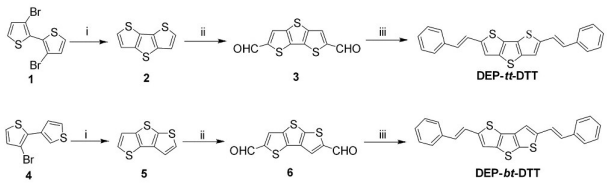

Scheme 1 Synthesis of **DEP-*tt*-DTT** and **DEP-*bt*-DTT**. i) *n*-BuLi (2.2 equiv), $(PhSO_2)_2S$ (1.05 equiv); ii) LDA (2.2 equiv), DMF (4.0 equiv); iii) $PhCH_2PPh_3Br$ (2.2 equiv), *t*-BuOK (3.0 equiv).

the same numbers and kinds of atoms in different structural arrangements. The varying of atoms arrangement will bring the changes of the physical and chemical properties. So it is necessary to study the relationship between the molecular structures of isomers and their OFETs performances, which will benefit us to further understand the essence of charge transport in organic semiconductors and to improve the devices performances.

Herein, as another isomer of **DEP-*bb*-DTT** and **DEP-*tt*-DTT**, 2,5-distyryl-dithieno[2,3-*b*:2',3'-*d*]thiophene (**DEP-*bt*-DTT**) was synthesized. The single crystal structures and OFETs based on these three isomers were investigated. Combining with the theoretical calculations, it can be confirmed that the positions of sulphur atoms play a decisive role for the conjugation extent of sulphur participation and the forms of intermolecular interactions, which affect the charge transport and OFETs performances.

Results and Discussion

Synthesis and characterization

DEP-*bb*-DTT was synthesized according to our previous report.[38] The synthesis of **DEP-*tt*-DTT** and **DEP-*bt*-DTT** is described in Scheme 1. The total yield after sublimation is 35% for **DEP-*tt*-DTT** and 31% for **DEP-*bt*-DTT**, respectively. All the intermediates were validated by NMR and MS. The target compounds **DEP-*tt*-DTT** and **DEP-*bt*-DTT** were confirmed by HRMS. The single crystals of **DEP-*bt*-DTT** (CCDC number 1414571) were obtained in the sublimation process.

Single crystals and intermolecular interactions

X-ray diffraction studies of the single crystal structure are shown in Figure 1. The **DEP-*bt*-DTT** molecule displays a quasi-bowed shape, which is similar to **DEP-*tt*-DTT** and **DEP-*bb*-DTT**.[37,38] The twisted angles between the terminal phenyl groups and the DTT plane in **DEP-*bt*-DTT** single crystal structures are 9.3° and 11.7°, respectively. There exist S–C and S–S intermolecular interactions between the neighbouring molecules of **DEP-*bt*-DTT**. And the molecules adopt the herringbone arrangement in their packing with the herringbone angle of 48.6°. Between the adjacent parallel molecules, π-π spacing is about 2.448 Å.

For detailed comparisons, Table 1 lists some structural parameters in the single crystals of these three isomers. It is obvious that the herringbone angle and π-π spacing in **DEP-*bt*-DTT** single crystals are lower than that in **DEP-*bb*-DTT,** but higher than that in **DEP-*tt*-DTT,** while the twisted angles in **DEP-*bt*-DTT** are higher than that in **DEP-*bb*-DTT,** but lower than that in **DEP-*tt*-DTT**. Furthermore, it should be also noticed that the intermolecular interactions in their single crystals of these three isomers are different. For **DEP-*tt*-DTT**, the intermolecular interactions consist of three S–C interactions between the sulphur atom on the middle thiophene unit (*bottom* position) and the three carbon atoms

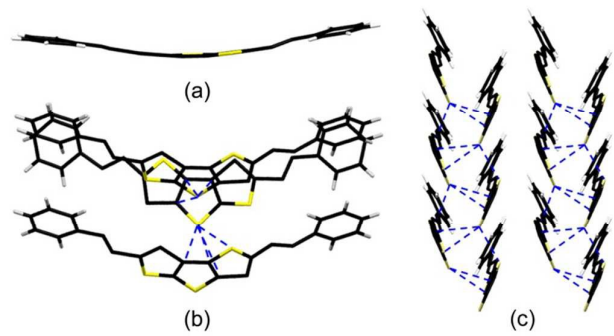

Figure 1. Molecular shape and intermolecular interactions in the single crystals of **DEP-*bt*-DTT**. (a) side view; (b) intermolecular interactions; (c) the packing pattern. The dashed line presents the close contact between atoms.

Table 1. The structural information of **DEP-*bb*-DTT**, **DEP-*bt*-DTT** and **DEP-*tt*-DTT** in their single crystals.

Materials	Twisted angle [c] (°)	herringbone angle [d] (°)	Intermolecular interaction [e]	*d* [f] (Å)
DEP-*bb*-DTT [a]	8.2 10.0	52.0	4 S–C (S–π)	2.575
DEP-*bt*-DTT	9.3 11.7	48.6	3 S–C/1 S–S	2.448
DEP-*tt*-DTT [b]	10.9 13.2	43.1	3 S–C/2 S–S	2.256

[a, b] The crystal data were downloaded from Cambridge Crystallographic Data Centre (CCDC-836921 for **DEP-*bb*-DTT** and CCDC-7116820 for **DEP-*tt*-DTT**). [c] The twisted angle is the angle between the plane of the terminal phenyl group and **DTT** unit. [d] The herringbone angle represents the angle between the neighbour molecules of herringbone arrangement in their single crystal structures. [e] The information of intermolecular interactions among the packing molecules. [f] The distance of π–π spacing.

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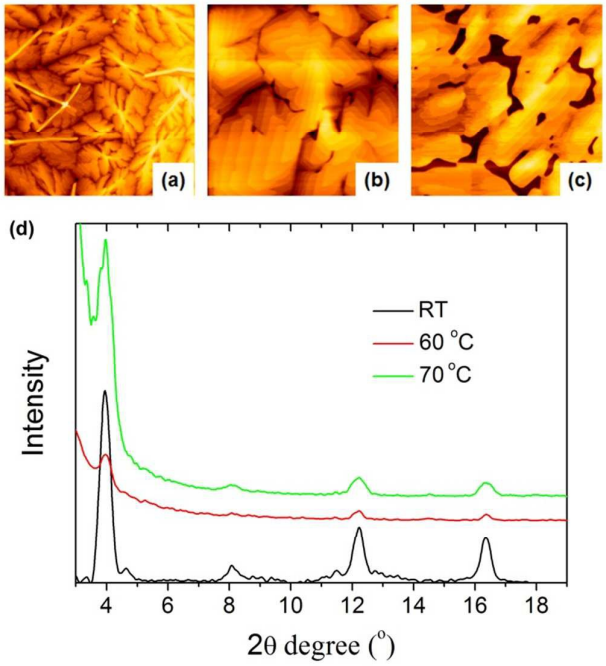

Figure 2. The topographical images: (a) RT, (b) 60 °C , (c) 70 °C and X-ray diffraction patterns of **DEP-*bt*-DTT** films at different substrate temperature.

on the middle thiophene unit in the neighbour molecule, and two S–S interactions between the sulphur atom at *bottom* position and the sulphur atoms on the other two thiophene units (*top* positions) in the neighbour molecule. As the positions of sulphur atoms varying from *top-bottom-top* in **DEP-*tt*-DTT** to *bottom-bottom-top* in **DEP-*bt*-DTT**, the same three S–C intermolecular interactions remain unchanged while two S–S intermolecular interactions in **DEP-*tt*-DTT** turn into one S–S intermolecular interaction between the sulphur atom at *bottom* position and the sulphur atom on the thiophene unit at the opposite position (*top* position) in the neighbour molecule. However, the S–S interaction disappears with four S–C (or S–π) interactions forming between the sulphur atom at *bottom* position and the whole four carbon atoms on the middle thiophene unit of the neighbouring molecule. Thus, it can be deduced that the varying of sulphur atoms positions can bring a disciplinary change not only for the molecular arrangements but also for the intermolecular interactions.

Topographical images and absorption properties of films

Topographical images of **DEP-*bt*-DTT** deposited at different substrate temperature (T_s) were investigated as shown in Figure 2. All the films possess high crystalline and the growth habit of **DEP-*bt*-DTT** shows layer-by-layer mode. The film at T_s of 60 °C (as shown in Fig. 2(b) is composed of large lamellar crystals with the average layer spacing around 2.0 nm, which is similar to that of **DEP-*bb*-DTT** and **DEP-*tt*-DTT**.[37,38] (The topographical images of **DEP-*tt*-DTT** and **DEP-*bb*-DTT** are shown in Figure *S20* in the supporting information.) This demonstrates that these three isomers have the same habits in the progress of their films growth.

X-ray diffraction patterns of **DEP-*bt*-DTT** films deposited at different T_s were also investigated. Fig. 2(d) shows the typical X-ray diffraction patterns of all films. All the films exhibit a series of peaks with multiple orders of reflection, which indicates that all these films are high crystalline even if they were deposited at T_s of RT. This is consistent with that of topographical images. According to the single crystal structure, the indices of crystallographic plane (*00l*) for **DEP-*bt*-DTT** were established. The interplanar spacing, calculated according to the Bragg's equation, is about 2.0 nm, which is consistent with that obtained for AFM and the half length of the molecular long axis in the single crystals. Therefore, it can be

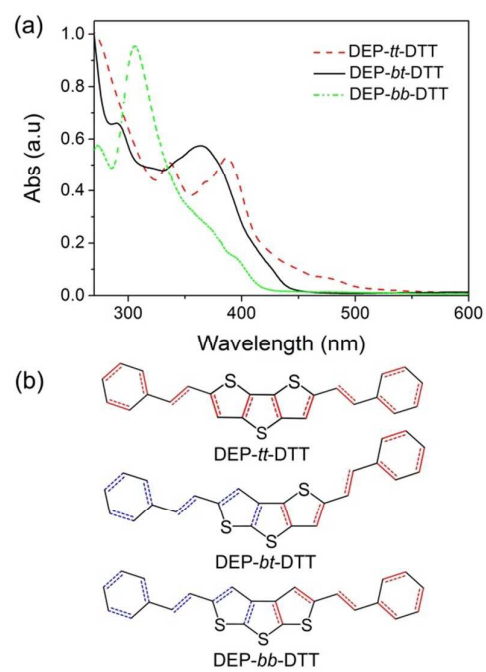

Figure 3. (a) Normalized UV–vis absorption spectra of **DEP-*tt*-DTT** (dashed line), **DEP-*bt*-DTT** (solid line) and **DEP-*bb*-DTT** (dashed with dots line) films deposited on quartz with thickness of 50 nm. (b) The conjugation way of these three isomers.

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Table 2. The characteristics of OFETs based on **DEP-*bb*-DTT**, **DEP-*bt*-DTT** and **DEP-*tt*-DTT**.

Materials	T_s (°C)	μ [a] (cm^2/Vs)	V_T [b] (V)	I_{on}/I_{off}
DEP-*tt*-DTT	RT	0.02	-25	10^4
	60	0.04	-30	10^4
	70	0.01	-35	10^4
DEP-*bt*-DTT	RT	0.04	-48	10^4
	60	0.1	-52	10^4
	70	0.03	-56	10^4
DEP-*bb*-DTT	RT	1.4	-66	10^5
	70	2.0	-60	10^5
	100	1.2	-66	10^5

[a, b] The average values from more than five parallel devices.

concluded that the molecular long axe of **DEP-*bt*-DTT** is almost perpendicular to the substrate. In the process of films growth, the array of the sample molecules would adopt the same way as that in their single crystals due to the intermolecular interactions. Thus it states that the molecular arrangement in **DEP-*bt*-DTT** films should be coincident with that in their single crystals. For **DEP-*tt*-DTT** and **DEP-*bb*-DTT**, X-ray diffraction patterns (as shown in Figure *S21* and *S22*) also indicate that their molecular arrangements are consistent with that in their single crystals, as discussed in Ref. [37] and [38].

Figure 3(a) illustrates UV-vis absorption properties of these three isomers films deposited on the quartz substrates with thickness of50 nm. The absorption peaks are 273 and 306 nm for **DEP-*bb*-DTT**, 291 and 364 nm for **DEP-*bt*-DTT**, 336 and 387 nm for **DEP-*tt*-DTT**, respectively. The onsets in absorption spectra are about 418 nm, 443 nm and 550 nm for **DEP-*bb*-DTT**, **DEP-*bt*-DTT** and **DEP-*tt*-DTT**, respectively. From **DEP-*bb*-DTT** to **DEP-*bt*-DTT**, then to **DEP-*tt*-DTT**, a distinct bathochromic-shift is observed in the absorption spectra. Generally, the absorption properties are closed to the molecular configuration and the conjugation extent. In these three isomers, all the molecules present a quasi-bowed shape. So the difference among the absorption properties can be attributed to the difference of the molecular conjugation extent. For **DEP-*tt*-DTT**, it shows complete conjugation through whole molecule with altering single and double bonds, while they are composed of two partial conjugations in **DEP-*bt*-DTT** and **DEP-*bb*-DTT** as shown in Fig. 3(b). The different way of conjugation may be result in the different extent of conjugation in these three isomers, which accounts for the distinct bathochromic-shift in the absorption spectra. Furthermore, this change also matches the varying rule of structural parameters in their single crystals as discussed above.

Field-effect characteristics

OFETs based on these three isomers were fabricated at the same conditions except the substrate temperatures (T_s). The characteristics of these OFETs at different T_s are listed in Table 2. Based on the films of **DEP-*bt*-DTT** with large lamellar crystals as shown in Fig. 2 (b), the higher μ of 0.1 cm^2/Vs was obtained. For **DEP-*bb*-DTT**, the values of μ are nearly equivalent to that of reports, while the values of μ for **DEP-*tt*-DTT** are lower than that of reports.[37] This may be attributed to the OTS-modified SiO_2/Si substrate in Ref. [37]. With carefully comparing the field-effect characteristics among OFETs based on these three isomers, it can be found that the values of μ increase from 0.04 to 0.1, then to 2.0 cm^2/Vs, and the absolute values of threshold voltage (V_T) increase from 30 to 52, then to 60 V, when the positions of sulphur atoms vary from *top-bottom-top* in **DEP-*tt*-DTT** to *bottom-bottom-top* in **DEP-*bt*-DTT**, then to *bottom-bottom-bottom* in **DEP-*bb*-DTT**. That is to say the characteristics of OFETs based on these three isomers also present regular changes with the positions of sulphur atoms varying. For these changes including intermolecular interactions, structural parameters in molecular packing, absorption and OFETs properties, they show regular variation on the macroscopic level, which is caused by a microscopic change in the positions of the sulphur atoms. It expects a deeply study to explain these changes.

Theoretical calculations

As discussed above, the changes in intermolecular interactions, structural parameters in molecular packing, absorption and OFETs properties, are closed to the positions of the sulphur atoms. Normally, it is well known that the lone electron pair of sulphur structural parameters in molecular packing, absorption and OFETs properties are closed to the positions of the sulphur atoms. Normally, it is well known that the lone electron pair of sulphur atom combine with the C=C double bonds of thiophene to form a large π conjugation system. For further understanding the role of sulphur atoms in these three isomers, the energy levels and the natural of bond orbitals charges (NBO) were analyzed by the theoretical calculations.[50-53] Figure 4 shows the distribution of electron cloud at the highest occupied molecular orbits (HOMO) level, the lowest unoccupied molecular orbits (LUMO) and NBO charges of sulphur atoms, C=C double bonds, phenyl and styryl groups. As shown in Fig.4, the distribution of electron cloud on the sulphur atoms in **DEP-*tt*-DTT** is very few, which maybe indicate the sulphur atoms scarcely participate in the molecular conjugation. For **DEP-*bt*-DTT**, the two sulphur atoms at the bottom-bottom positions completely contribute to the molecular conjugation, while the other sulphur atom at the top position only partly contribute to the molecular conjugation. On the contrary, all the sulphur atoms almost completely participate in the molecular conjugation in **DEP-*bb*-DTT**. So it can be deduced that the contribution extents of the sulphur atoms to the molecular conjugation are different in these three isomers. In fact, the contribution extents of the sulphur atoms to the molecular conjugation can also be confirmed by the NBO charges. As marked in Fig.4, the NBO charges of sulphur atoms are 0.466, 0.447 and 0.466, and the total value is 1.379 in **DEP-*tt*-DTT**. For **DEP-*bt*-DTT**, the NBO charges of sulphur atoms are 0.463, 0.471 and 0.465, and the total value is 1.399. The NBO charges of sulphur atoms in **DEP-*bb*-DTT** are 0.461, 0.495 and 0.461 with the total value of 1.417. It is very obvious that the contribution extents of the sulphur atoms are different among these three isomers.[52] As a result, the phenyl and styryl groups also show different contribution to the molecular conjugation as shown in Fig. 4. Furthermore, it is because of these different contribution extents of sulphur atoms, so

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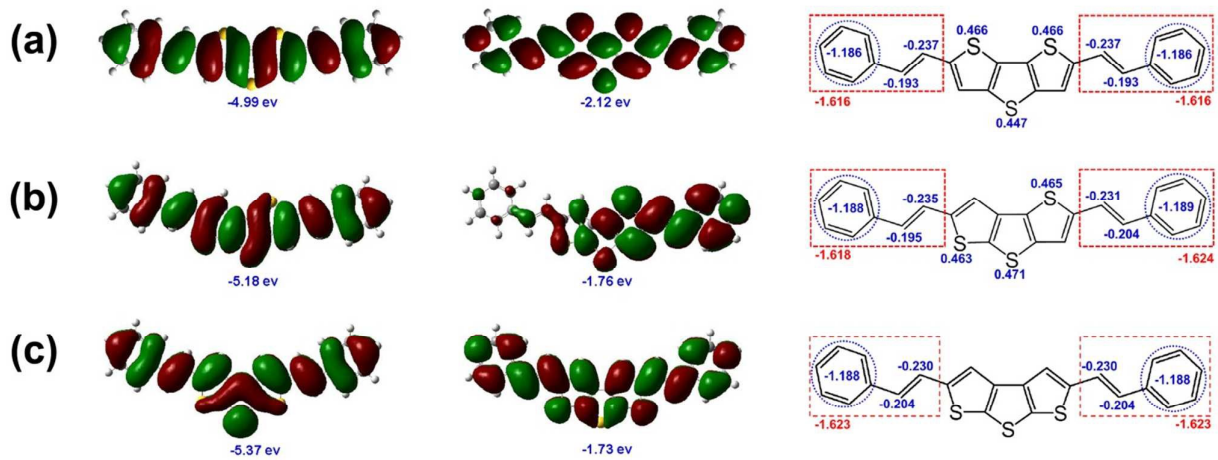

Figure 4. The distribution of electron cloud at the highest occupied molecular orbitals (HOMO) level (left column), the lowest unoccupied molecular orbits (LUMO) and the natural of bond orbitals charges (NBO) (right column) obtained from the theoretical calculations: (a) **DEP-*tt*-DTT**; (b) **DEP-*bt*-DTT** and (c) **DEP-*bb*-DTT**.

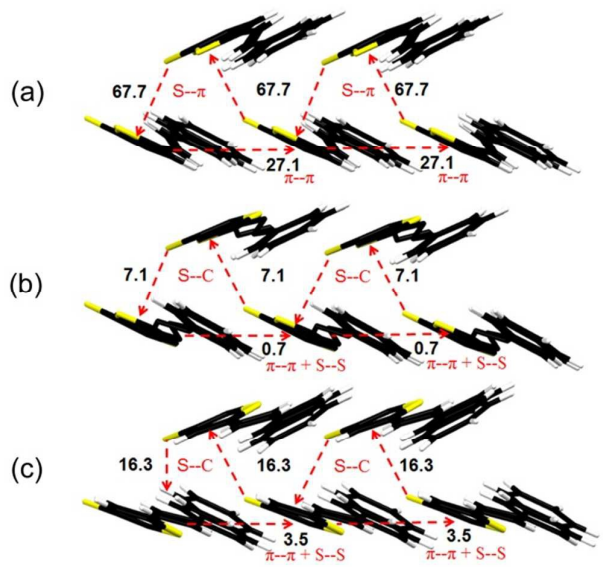

Figure 5. The charge hopping pathway and the values of holes transfer integrals between the neighboring molecules of **DEP-*bb*-DTT** (a), **DEP-*bt*-DTT** (b) and **DEP-*tt*-DTT** (c) taken from the single crystal structure.

the intermolecular interactions present various formations. For **DEP-*bb*-DTT**, it can form S–π intermolecular interaction between the neighbouring molecules due to the high NBO charge of the middle sulphur atom. In spite of the high NBO charge of the middle sulphur atom, there does not appear S–S intermolecular interaction due to the large distance between the molecules in **DEP-*bb*-DTT.** However, there present the coexisting of S–C and S–S intermolecular interactions under the coefficient effect of high NBO charges of the middle sulphur atoms and the short distances between the molecules in **DEP-*bt*-DTT** and **DEP-*tt*-DTT**.

In order to further understand the effect of the intermolecular interactions on the charge transport in OFETs, the charges transfer integrals[54-57] were done on the directions of intermolecular interactions and π–π stacking as shown in Figure 5. The higher values emerge on the directions of S–C (or S–π) intermolecular interactions in three isomers, which mean that S–C (or S–π) intermolecular interactions are the most efficient way for the charge transport. Compared the values of transfer integrals on the direction of π–π stacking in these three isomers, the values of transfer integrals are highest in **DEP-*bb*-DTT** and lowest in **DEP-*bt*-DTT**. As mentioned above, there also exists one S–S intermolecular interaction and two S–S intermolecular interactions on the direction of π–π stacking in **DEP-*bt*-DTT** and **DEP-*tt*-DTT**, respectively. So it may be inferred that: 1) S–S intermolecular interaction also has a weak effect for improving the charge transport; 2) S–S intermolecular interaction can trenchantly reduce the effect of π–π intermolecular interaction on the charge transport when they are on the same direction. On the other hand, the absolute values of VT reduce gradually with the strengthening of S–S intermolecular interaction from **DEP-*bb*-DTT** to **DEP-*bt*-DTT**, then to **DEP-*tt*-DTT**.

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Conclusions

In summary, **DEP-*bt*-DTT**, as a new isomer of **DEP-*bb*-DTT** and **DEP-*tt*-DTT**, was synthesized. Combining the single crystal structures, the properties of OFETs and the theoretical calculations, it was found that the positions of sulphur atoms play an important role on the formation of intermolecular interactions and devices performances in these three isomers. With the positions of the sulphur atoms varying from *top-bottom-top* in **DEP-*tt*-DTT** to *bottom-bottom-top* in **DEP-*bt*-DTT**, then to *bottom-bottom-bottom* in **DEP-*bb*-DTT**, the contribution of sulphur atoms to the molecular conjugation increases, together with the twisted angles of phenyl groups contorting from **DTT** plane decreasing and the herringbone angle and π–π spacing increasing. Due to the changing of the contribution extent to the molecular conjugation, the sulphur atoms possess different NBO charges, which result in the various intermolecular interactions between the neighbouring molecules in these three isomers. All the intermolecular interactions including S–C (or S–π) and S–S benefit for the charge transport, but S–S intermolecular interaction can sharply weaken the effect of π–π intermolecular interaction on the charge transport when they are on the same direction. This will help us to design more new organic semiconductors with high μ by improving the contribution of the sulphur atoms to the molecular conjugation.

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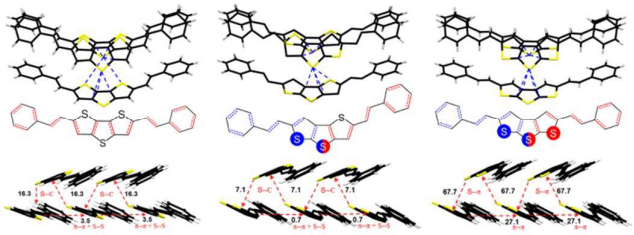

The sulfur atoms positions in three isomers play an important role on the intermolecular interactions and OFETs performances.

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