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Graphical Abstract

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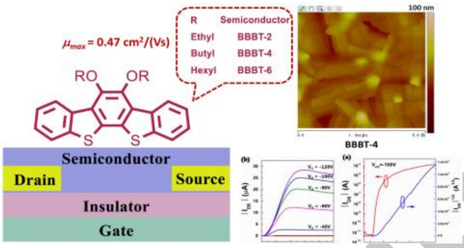

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Structure-Property Relationships of Benzo[2,1-*b*:3,4-*b'*]*bis*[1]benzothiophenes for Organic Field Effect Transistors

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ABSTRACT

A series of novel benzo[2,1-b:3,4-b']bis[1]-benzothiophene (BBBT) derivatives with different side-chains were synthesized and characterized. And their mobility properties were evaluated based on their active layers in OFETs devices. By means of simple thermal annealing, the devices based on BBBT-4 and BBBT-6 exhibited typical p-type FETs behavior with average hole mobilities of 0.28 and 0.124 cm2 V−1 s−1, respectively. Furthermore, the structure–property relationships of these semiconductors were also investigated by XRD and AFM.

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1. Introduction

Organic semiconductors are promising active layers for the new-generation electronics, attributed to their intriguing advantages of low-cost, light-weight, and flexibility.[1, 2] Over the last decades, great progress has been made in the development of OFETs and a large number of organic semiconductors have been developed for OFET applications.[3-5]

Previously, acenes have been widely explored as efficient charge transport semiconductors for OFETs.[6] Meanwhile, a large number of thienoacenes with good charge transport mobility have been developed for OFET applications because of their desirable close packing in the solid state, which arising from their rigid and planar structures and the desirable intermolecular S•••S, S•••H, and S•••π interactions. Besides, the OFETs based on thienoacenes also exhibited relatively higher air stability as compared to the acene-based devices because of their lower HOMO energy levels.[7, 8] For instance, dibenzothiopheno[6,5-*b*:6′,5′-*f*]thieno[3,2-*b*]thiophene (**DBTTT**) has been developed by Lee and coworkers, exhibiting a champion hole mobility of 19.3 cm^2·V^{-1}·s^{-1} in OFET fabricated by vacuum deposition.[9] It has also been demonstrated that molecular engineering strategy using various alkyl chains incorporated onto the conjugated backbone is an effective means to tune the solubility and morphology, and thus to enhance the processibility and the charge carrier mobility of the organic semiconductors.[10] Nevertheless, relatively scarce organic semiconductors with alkyl chains incorporated laterally have been investigated as compared to those end-capped with alkyl chains.

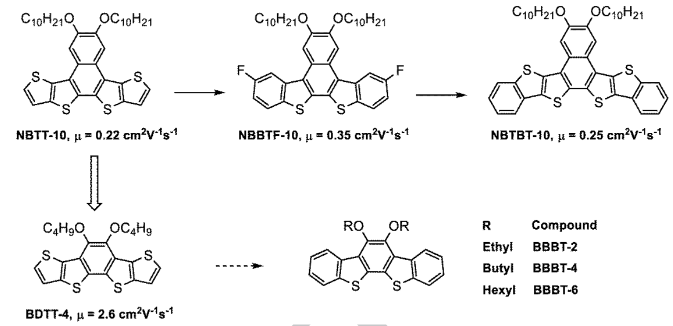


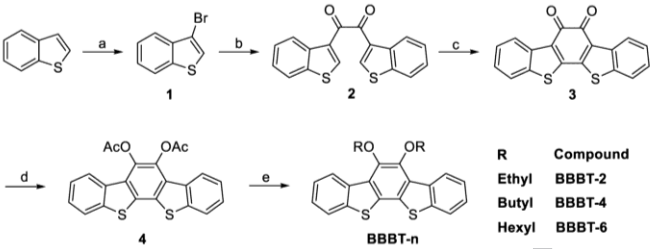
Figure 1. Molecular structures of laterally alkyl-substituted thienoacenes for OFET applications.

In our previous studies, several series of thienoacene-based semiconductors with alkyl side-chains have been synthesized and investigated including **BDTT**, **NDTT**, **NBTBT**, and **NBBT**.[11-14] In these works, the benzo semiconductors show better mobility performance than the naphtho ones, and the mobility properties of the semiconductor are affected by the lateral alkoxy groups. With these conclusions in mind, we reasoned that the mobility performance of **NBBT** could be improved by replace the terminal thiophene with benzene ring. Therefore, in this contribution, a series of air-stable benzo[2,1-*b*:3,4-*b'*]bis[1]benzothiophenes (**BBBT-n**) derivatives were designed and synthesized, in which different alkoxy groups were employed to tune the morphology of the semiconductors on the substrate. Their performances in OFETs have also been investigated, and **BBBT-4** was found to exhibit the best OFET performance with a hole carrier mobility of 0.47 cm^2·V^{-1}·s^{-1} and an on/off current ratio of 10^8. (Figure 1)

2. Results and discussion

2.1. Materials and Synthesis

Scheme 1 Synthesis of **BBBT-2**, **BBBT-4** and **BBBT-6**



Reagents and conditions: (a) NBS, CHCl$_3$, AcOH, 83%; (b) *n*-BuLi, CuBr, LiBr, oxalyl chloride, THF/ethyl ether, 54%; (c) FeCl$_3$, DCM, 78%; (d) Zn, (CH$_3$CO)$_2$O, NEt$_3$, DCM, 59%; (e) Cs$_2$CO$_3$, RX (X = Br, I), CH$_3$CN, 72-75%.

The **BBBT-n** derivatives were synthesized according to the synthetic route depicted in Scheme 1. Selective bromination of benzo[*b*]thiophene by means of NBS produced 3-bromobenzo[*b*]thiophene, **1** in a good yield. Double nucleophilic substitution reaction of oxalyl chloride with freshly prepared lithium organocuprate of **1** yielded diketone **2**. Subsequent ring-closing reaction catalyzed by FeCl$_3$ gave the fused-ring diketone **3** in a good yield. The cascade reaction of reduction and acetylation led to the formation of acetylated benzodithienothiophene **4** in a moderate yield. The **BBBT-n** series were then synthesized according by the reaction of acetylated intermediate **4** and the corresponding alkyl halide in the presence of Cs$_2$CO$_3$ as a base. All the **BBBT-n** derivatives were fully characterized by ^{1}H NMR, ^{13}C NMR, HRMS and the spectroscopic data are in good agreement with the proposed structures. All the details are listed in the supporting information.

2.2. Thermal, optical and electrochemical properties

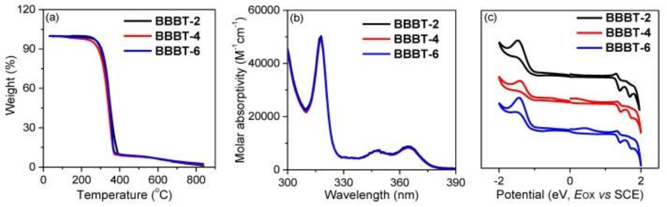


Figure 2. TGA, UV-vis absorption spectra, and CV traces of **BBBT**s

Table 1. Summaries of optical and electrochemical measurements of **BBBT**s

Compound	$E_g^{a,b}$ (eV)	$E_{oxd}^{onset\ c}$ (eV)	E_{HOMO}^{d} (eV)	E_{LUMO}^{e} (eV)
BBBT-2	3.18	1.3	-5.6	-2.4
BBBT-4	3.18	1.3	-5.6	-2.4
BBBT-6	3.17	1.3	-5.6	-2.4

^{a}Measured in DCM. ^{b}Estimated from the absorption edge of absorption in DCM, E_g = (1240/λ_{onset}) eV. ^{c}Ferrocene was used as the external standard, $E_{1/2}$ (Fc/Fc$^+$) = 0.47 V *vs.* SCE. ^{d}Calculated from the first oxidation potential with ferrocene (4.8 V *vs.* vacuum). HOMO = -4.33 - E_{oxd}^{onset} ^{e}LUMO = HOMO + E_g.

The thermal stabilities of **BBBT**s were estimated by thermogravimetric analysis (TGA). As shown in **Figure 2 (a)**, all these compounds exhibited good thermal stability with decomposition temperature of around 295 °C. In order to investigate the effects of different alkoxy groups on the optoelectronic performance, UV-vis absorption spectra of **BBBT**s were measured in CH$_2$Cl$_2$ solution, as shown in **Figure 2 (b)**. All these compounds exhibited strong absorption bands in the range of 290-330 nm and weak absorption bands in the range of 340-380 nm, corresponding to an optical bandgap of 3.28 eV. Furthermore, these three compounds exhibited approximately identical absorption bands, indicating that the alkoxy substituents have negligible effect on the electron distribution of πconjugation backbone. Cyclic voltammetry was performed to estimate the electrochemical properties of **BBBTs**, using ferrocene as an external standard, as shown in **Figure 2 (c)**. The HOMO energy levels were calculated from the onset of the oxidation waves (**Table 1**). All of **BBBTs** exhibited HOMO energy levels of around -5.6 eV, lower than that of pentacene (−5.0 eV), indicating good air-stability than pentacene for OFET applications.

2.3. Device properties for OFETs.

Table 2. Summaries of OFET characteristics based on **BBBTs**

Compound	μ_{avg} (cm^2/(Vs)) ^{a}	μ_{max} (cm^2/(Vs))^b	I_{on}/I_{off}	V_T (V)
BBBT-2	—	—	—	—
BBBT-4	0.28	0.47	$10^{7\sim8}$	-15
BBBT-6	0.124	0.134	$10^{6\sim7}$	-13

^{a}More than 10 devices were measured in air. ^{b} Measured in N$_2$.

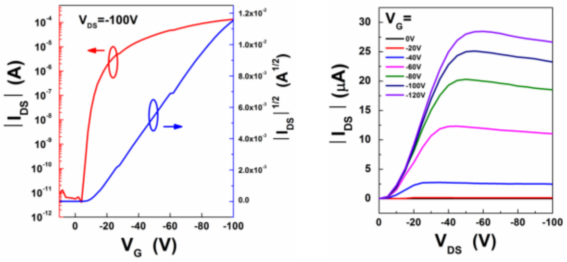


Figure 3. Typical electrical characteristics of the **BBBT-4** based OFET: (a) transfer and (b) output characteristics

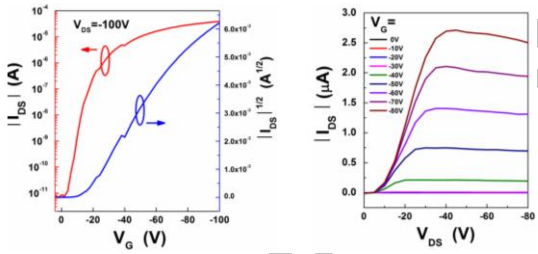


Figure 4. Typical electrical characteristics of the **BBBT-6** based OFET: (a) transfer and (b) output characteristics

BBBT-4 and **BBBT-6** based OFETs in BGBC configuration were prepared by vacuum deposition (6~10 Å/min) onto Si/SiO$_2$ substrate, with two gold electrodes. The mobility performance was measured under ambient conditions and the results were summarized in **Table 2**. The thin films of **BBBT-4** and **BBBT-6** showed typical p-type semiconducting characteristics. Their representative transfer and output characteristics are showed in **Figures 3** and **4**. On the contrast, **BBBT-2** showed poor ability to form a homogeneous film, even distinguished by naked eyes, due to its high tendency to crystallize caused by the very short lateral alkyl chains.[15] As a result, **BBBT-2** has not exhibited any mobility performance in the device characterization. On the other hand, **BBBT-4** based devices exhibited a hole carrier mobility up to 0.28 cm^2/(Vs) with a high on/off current ratio of $10^{7\text{-}8}$. With an increase in the length of alkyl chains, the carrier mobility of **BBBT-6** based OFETs decreased to 0.124 cm^2/(Vs) as well as a reduction in on/off current ratio of $10^{6\text{-}7}$. The decrease in the carrier mobility might be due to the longer alkyl chains, which could form insulator layers among the stacks, and thus leading to the adverse effect to the charge transport of the semiconductors.[16] These results highlight the importance of the lateral chain length optimization for a high-performance OFET.

2.4. XRD and AFM characterizations

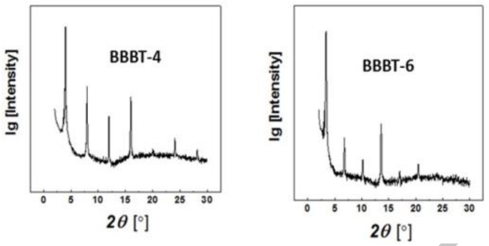


Figure 5. X-ray diffraction patterns of **BBBTs** thin films

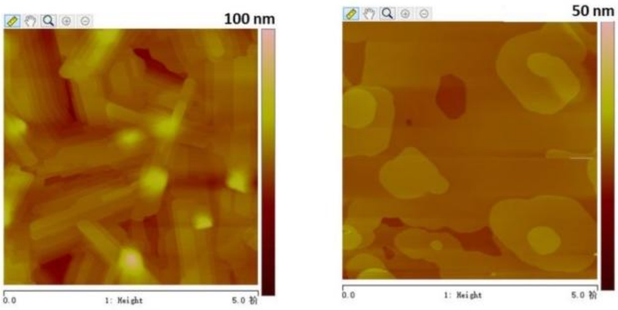
Table 3. Summaries of X-ray diffraction of the thin films deposited on Si/SiO$_2$

Compound	Primary Peak (°) ^{a}	*d*-scaling (Å)^b
BBBT-4	3.99	22.1
BBBT-6	3.36	26.3

^{a}Determined by XRD patterns.

^{b}Estimated from primary diffraction peaks of the corresponding films.

To investigate the relationships between film crystallinity/morphology and the OFET performance, out-of-plane X-ray diffraction (XRD) were conducted on the films of **BBBTs**. The XRD patterns are shown in **Figure 5** and the results are summarized in **Table 3**. **BBBT-4** exhibited a primary diffraction peaks at 3.99 °, corresponding to the *d*-spacing of 22.1 Å, while **BBBT-6** exhibited a decreased primary diffraction peaks of 3.36 ° with the *d*-spacing raising up to 26.3 Å, which is attributed to the longer alkyl side chains.



BBBT-4 **BBBT-6**

Figure 6. AFM images of **BBBT-4** and **BBBT-6** thin films.

Furthermore, atomic force microscopy (AFM) investigation was carried out to study the morphology of the thin-films of **BBBT-n**. The AFM images of **BBBT-4** and **BBBT-6** exhibit distinctively different morphologies (**Figure 6**). The film of **BBBT-6** exhibited globular morphologies with large grain size. On the other hand, the thin-film of **BBBT-4** exhibited rod-shape morphology with grain boundaries and better ordering, which would enhance the mobility performance.

3. Conclusions

In summary, we have designed and synthesized benzo[2,1-*b*:3,4-*b'*]bis[1]benzothiophene (**BBBT**) derivatives for OFET applications, in which alkoxy substituents with different lengths were employed to tune the morphologies of the semiconductor films. As a result, **BBBT-4** based devices showed the best hole carrier mobility up to 0.47 cm^2/(Vs), which was consistent with its thin-film morphology characteristics. These findings not only demonstrate chain length engineering is a reliable method to improve the morphology of semiconductor films, but also highlight the potential of benzodithienothiophene-containing molecules with alkoxy side-chains to achieve high OFET performance. Furthermore, benzodithienothiophene can serve as the building block for the construction of high-mobility semiconducting polymers.

Acknowledgments

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Supplementary Material

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HIGHLIGHTS:

A series of **BBBTs** with different side chains were designed and synthesized.

The mobility properties of **BBBTs** film were evaluated in OFETs device.

The effect of side chains on the mobility properties were investigated by XRD and AFM.