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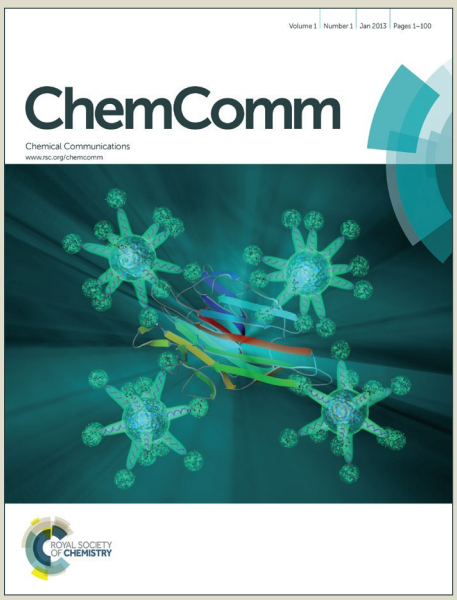

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ARTICLE TYPE

High-Performance Organic Field-Effect Transistors Based on Single-Crystalline Microribbons of a Two-Dimensional Fused Heteroarene Semiconductor

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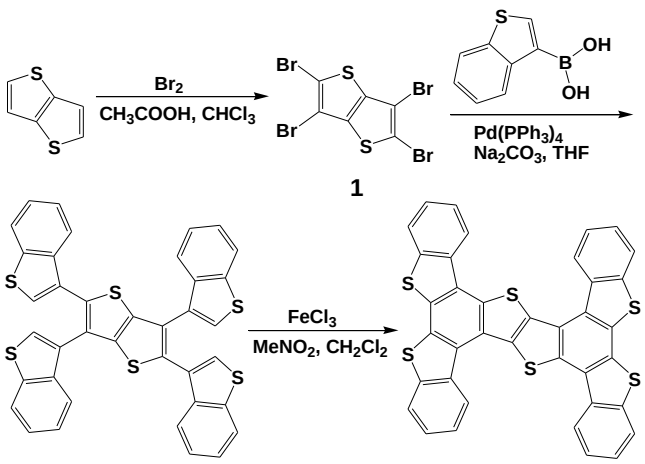
A novel two-dimensional organic semiconductor material [1]benzothieno[3,2‐b][1]benzothieno[2,1-b:3,4-b':6,5-b'':7,8-b''']tetra(benzothiophene) (BTBTTBT) which largely extending the scope of π-conjugated framework of heteroarene through "H" configuration was synthesized. The thermal, optical and electrochemical properties were investigated. The 2D molecule is easy to grow single-crystalline microribbons by physical vapor transport method which evidenced by the XRD, SEM and TEM. The single-crystalline OFET devices were fabricated based on the individual BTBTTBT microribbon and the remarkable high mobility of 17.9 $cm^2V^{-1}s^{-1}$ and on/off ratios over 10^7 could be achieved.

In the past two decades, remarkable progress has been made in developing organic semiconductors with diverse molecular structures,[1] and the hole mobility is already as high as 40 $cm^2V^{-1}s^{-1}$ in air.[2] Nevertheless, few of the reported materials meets all of the requirements for commercial application of the organic field-effect transistors（OFETs）, and further development of organic semiconductor materials with excellent performance is still desired in the future electronics industry. Efficient charge transport in molecular solids requires charge carriers to move easily between the molecules.[3] The geometric features of molecule play important roles in intermolecular interactions and supramolecular self-assembly, thus significantly influence the charge transfer between adjacent molecules in organic semiconductors. The linear thioacenes have been demonstrated high mobility due to their rigid, coplanar and π-conjugated framework structure as well as the S···S interactions.[4] It is plausible to design the molecules with larger π-electronic cores to improve the FET performance, however, the present experimental results indicate that the largely π-extended thienoacenes cannot always afford good performances as organic semiconductors.[5] On the other hand, the two-dimensional (2D) configuration opens a door for extending the scope of π-conjugated framework efficiently, and therefore enhancing the intermolecular charge transport due to the potential π-π stacking by effectively controlling over the molecular orientation in the solid state.[6]

In earlier work, we adopted the starphene[7] and butterfly[8] configuration to synthesize the 2D molecules respectively. Both the compounds are easy to assemble into micro- and nanoscale organic crystals due to the strong π-π stacking between the 2D molecules. The single-crystal transistors devices based on their micro- and nanostructure demonstrated high mobility up to 0.56 $cm^2V^{-1}s^{-1}$ and 2.62 $cm^2V^{-1}s^{-1}$ respectively. In this study, we proposed a "H" configuration to construct novel 2D organic semiconductor molecule which using the thieno[3,2-b]thiophene as the bridge part fused with two five-member thienoacenes, namely [1]benzothieno[3,2‐b][1]benzothieno[2,1-b:3,4-b':6,5-b'':7,8-b''']tetra(benzothiophene) (BTBTTBT). The extending π-conjugated 2D molecule is very beneficial to grow single-crystalline microribbons which evidenced by the X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopic (TEM). The OFET devices based on the single-crystalline microribbons exhibit excellent performance with the average mobility of 5.57 $cm^2V^{-1}s^{-1}$ for the fabricated thirty transistors and on/off ratios over 10^7.

The synthetic route of BTBTTBT was depicted in Scheme 1 which includes three steps from commercially available thieno[3,2-b]thiophene as starting material. Thieno[3,2-



Scheme1. Synthetic route of BTBTTBT.

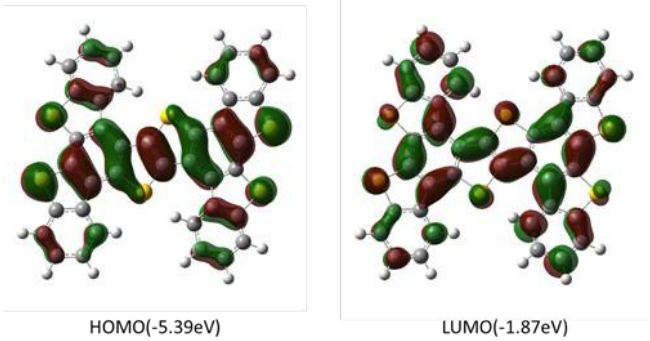


Fig. 1 HOMO and LUMO orbitals of BTBTTBT obtained by using DFT calculations.

b]thiophene was brominated to give **1** according to a known procedure described in the literature.[9] Then **2** was prepared by Suzuki coupling reaction between **1** and benzo[b]thiophen-3-ylboronic acid. After oxidative cyclization with ferric chloride,[10] a 2D fused-ring compound BTBTTBT was constructed via thienyl-thienyl carbon-carbon bond formation. BTBTTBT is not soluble in common organic solvents due to the highly π-extended, rigid, and nearly planar structures without any substituents at the periphery. Thus the pure product was obtained by vacuum subliming and its characterizations were done with high resolution mass spectrometry and elemental analysis.

BTBTTBT exhibits very high thermal stability which investigated by thermal gravimetric analysis (TGA) and the thermal decomposition temperature is over 580 ℃ under nitrogen atmosphere. The UV-vis spectrum of BTBTTBT was examined by a solid thin film vacuum-deposited on quartz due to the poor solubility (shown in Fig. S1). The optical energy bandgap of BTBTTBT estimated from the maximal absorption edge in film phase was 2.68 eV.

The cyclic voltammetry of BTBTTBT was done in dichloromethane solution containing 0.1 M tetrabutylammoniumhexafluorophosphate ($TBAPF_6$) as the supporting electrolyte. A reversible oxidation peak was

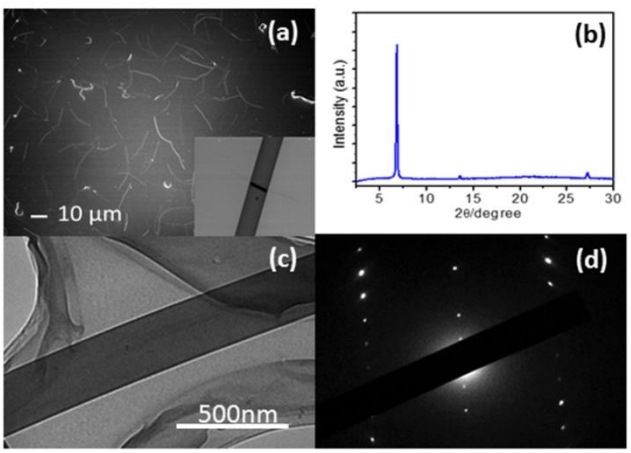


Fig. 2 (a) SEM images of BTBTTBT microribbons and the electrodes formed by the ‘‘organic ribbon mask technique’’ (insert), (b) XRD patterns of BTBTTBT microribbons on an OTS modified SiO_2, (c) TEM image of a fragment of the single-crystalline BTBTTBT microribbons, and (d) its corresponding electron diffraction pattern.

obverseved at $E_{1/2}$=+1.27 V (shown in Fig. S2) which indicates the good stability of BTBTTBT radical. The HOMO level of BTBTTBT determined by using the onset position (1.06 V) of the oxidation peak was -5.46 eV.[11] To gain deeper insight into the electronic structures of the 2D fused-ring BTBTTBT, molecular-orbital (MO) calculations of the HOMO and LUMO levels were performed by using the density functional theory (DFT) method at (B3LYP, 6-31G(d,p)) level (Fig. 1). The simulated result demonstrates that the central bridge part distributes more electron cloud and the distribution directions of HOMO and LUMO orbits are different. The theoretical HOMO (-5.39 eV) level is close to that estimated by cyclic voltammetry.

OFETs based on single crystals prepared by physical vapor transport (PVT) method generally exhibit a higher performance than other methods.[12] Single-crystalline microribbons of BTBTTBT were deposited onto the OTS-treated SiO_2 /Si substrate by PVT method under argon atmosphere. The images of microribbons and the electrode formed by an ‘‘organic ribbon mask technique’’[13] are observed by SEM and shown in Fig. 2a. The X-ray diffraction (XRD) measurement reveals a very strong diffraction peak at 2θ=6.86 degree (the corresponding d- spacing is12.87 Å, Fig. 2b), which indicates that the microribbons possess highly degree crystallinity. TEM observation of the BTBTTBT microribbons (Fig. 2c) demonstrated the regular shape, and

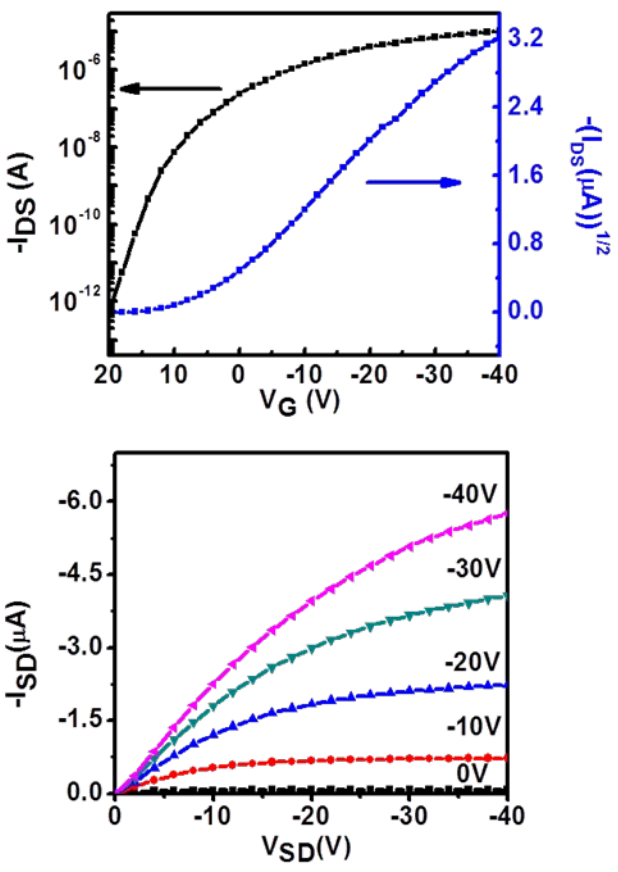


Fig. 3 Transfer (top) and output (down) characteristics of OFET devices based on the BTBTTBT single-crystalline microribbon.

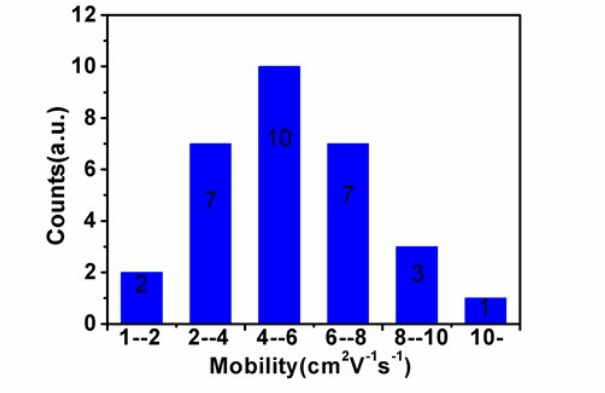


Fig. 4 Distributions of the mobility based on thirty OFET devices.

the corresponding selected-area electron diffraction (SAED) pattern (Fig. 2d) shows sharp and well-defined reflection spots, which confirms the single crystallinity of the microribbons.

The field-effect transistors based on the single-crystalline microribbons of BTBTTBT were fabricated by using ''organic ribbon mask technique'' with the gold as both source and drain electrodes. The OFET performances were measured in air, and the typical transfer and output characteristics are depicted in Fig. 3. All of the devices exhibited p-type semiconductor behavior and Fig. 4 shows the distribution of the hole mobility for the fabricated thirty transistors and the average mobility is as high as 5.57 $cm^2V^{-1}s^{-1}$. The average threshold voltage is 8.5 V and the average on-off ratio is greater than 10^7. The highest mobility of up to 17.9 $cm^2V^{-1}s^{-1}$ could be achieved. The high OFET performance may be result from the strong π-π stacking interactions between the 2D π-conjugated molecules and S ··S contacts owing to the sulfur atoms positioned at the molecular periphery.[14] The detailed relationship between the propeties and structure is still need to clarify by further experiments. However, our experimental results suggest that it is an efficient way for developing high performance semiconductor materials through the 2D "H" configuration to assemble thienoacenes.

In conclusion, by extending the scope of π-conjugated framework of heteroarene through "H" configuration, a novel 2D organic semiconductor material BTBTTBT is synthesized. The 2D molecule is easy to grow single-crystalline microribbons which evidenced by the XRD, SEM and TEM. The OFET devices were fabricated based on the single-crystalline BTBTTBT microribbons and the average mobility is as high as 5.57 $cm^2V^{-1}s^{-1}$ and on/off ratios over 10^7. Our results confirm this strategy for developing high performance semiconductor materials through using the largely π-extended 2D configuration.

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Notes and references

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