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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 cm²V⁻¹s⁻¹ and on/off ratios over 10⁷ could be achieved.

In earlier work, we adopted the starphene⁷ and butterfly⁸ 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 cm²V⁻¹s⁻¹ and 2.62 cm²V⁻¹s⁻¹ respectively. In this study, we proposed a “H” configuration to construct novel 2D organic semiconductor molecule which using the thiene[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 cm²V⁻¹s⁻¹ for the fabricated thirty transistors and on/off ratios over 10⁷.

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

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Scheme 1. Synthetic route of BTBTTBT.
b) Thiophene was brominated to give 1 according to a known procedure described in the literature. Then 2 was prepared by Suzuki coupling reaction between 1 and benzo[b]thiophen-3-ylboronic acid. After oxidative cyclization with ferric nitrate, 2 is 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 °C 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 (TBAPF₆) as the supporting electrolyte. A reversible oxidation peak was observed at E₁/₂=+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. 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 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. Single-crystalline microribbons of BTBTTBT were deposited onto the OTS-treated SiO₂ /Si substrate by PVT method under argon atmosphere. The images of microribbons and the electrode formed by an “organic ribbon mask technique” 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
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 BTBTFTBT 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 cm²V⁻¹s⁻¹. The average threshold voltage is 8.5 V and the average on-off ratio is greater than 10⁷. The highest mobility of up to 17.9 cm²V⁻¹s⁻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. The detailed relationship between the properties 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 BTBTFTBT 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 BTBTFTBT microribbons and the average mobility is as high as 5.57 cm²V⁻¹s⁻¹ and on/off ratios over 10⁷. 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


