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

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General. All reagents and chemicals are purchased from commercial sources and used without further purification. Tetrabromothieno[3,2-b]thiophene was synthesized according to the literatures.[20] Mass spectrometry was performed on a micrOTOF QII (Q-TOF) from Bruker Daltonics (Billerica, MA, USA). Elemental analyses were performed by the elementarvario III. Thermogravimetric analysis (TGA) was carried out on a PERKIN ELMER TGA7. The UV-vis spectrum was obtained on a JΛSCO V-570 UV/vis spectrometer. Cyclic voltammeter (CV) was run on a CHI660C electrochemistry station at a scan of 100 mV/s. The indium tin oxide (ITO) coated glass was used as the working electrode and Ag/AgCl as a reference electrode. The BTBTTBT was deposited onto the ITO electrode by evaporation under vacuum before measured. X-ray diffraction (XRD) measurements were carried out in the reflection mode using a 2-kW Rigaku X-ray diffraction system. Scanning electron microscopy (SEM) images were obtained with a Hitachi S-4300 SE (Japan), and TEM and SAED measurements were carried out on a JEOL 2010 (Japan).

Single crystal transistor device fabrication

The single-crystalline microribbons of BTBTTBT were grown onto OTS-treated SiO_2 /Si substrate by physical vapor transport method in a horizontal tube furnace. The furnace temperature was increased to 460 ℃ and then kept for 4 h. Then the drain-source (D-S) gold contacts were fabricated on the microribbon by thermal evaporation, using an organic ribbon as shadow mask. The masks used here were micrometer- or sub-micrometer ribbons of an anthracene derivative.[24] The characteristics of the OFET were performed using a Keithley 4200-SCS semiconductor parameter analyzer under ambient conditions.

Synthesis of 2,2',3,3'-Tetra-(3''-benzothieno)thieno[3,2-b]thiophene, 2

To a solution of tetrabromothieno[3,2-b]thiophene (1, 455 mg, 1 mmol) in degassed THF (80 mL) was added $Pd(PPh_3)_4$ (400 mg) and aqueous Na_2CO_3 (2 M, 40 mL). After degassed again, the benzothiophene-3-boronic acid (1.78 g, 10 mmol) was added and the mixture was refluxed for 24 h under argon atmosphere. After cooled to room temperature, the reaction mixture was filtered by Busher funnel to give a white solid as product 3 (600 mg, 90%). HRMS: m/z 667.9889 (calcd), 667.9874 (found).

Synthesis of [1]benzothieno[3,2-b][1]benzothieno[2,1-b:3,4-b':6,5-b'':7,8-b''']tetra(benzothiophene), BTBTTBT, 3

Compound 2 (668 mg, 1 mmol) was dissolved in dry dichloromethane (700 ml) in a 1000 mL three-necked flash. The iron (III) chloride (1.5 g) solution of nitromethane (10 ml) was added slowly at room temperature and bubbled continuously with argon through the reaction process. The mixture was stirred overnight and then quenched by methanol. The precipitate was collected by filtration and washed with water, methanol and dichloromethane successively. The crude product was purified by vacuum subliming to afford a yellow powder solid as the pure BTBTTBT (400 mg, 60%). HRMS: m/z 663.9576 (calcd), 663.9569 (found). Anal.Calcd for $C_{38}H_{16}S_6$: C, 68.64; H, 2.43; S, 28.93. Found: C, 68.58; H, 2.36.

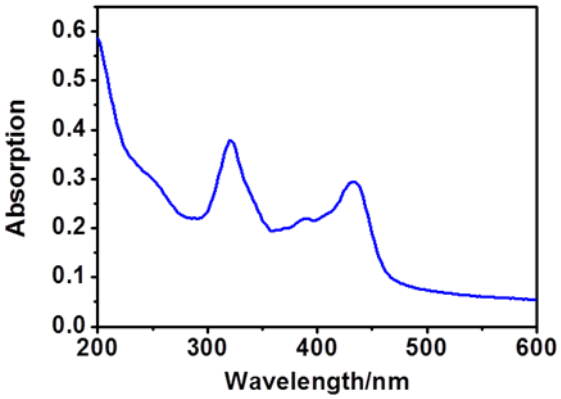

Fig. S1 UV-vis absorption spectrum of BTBTTBT.

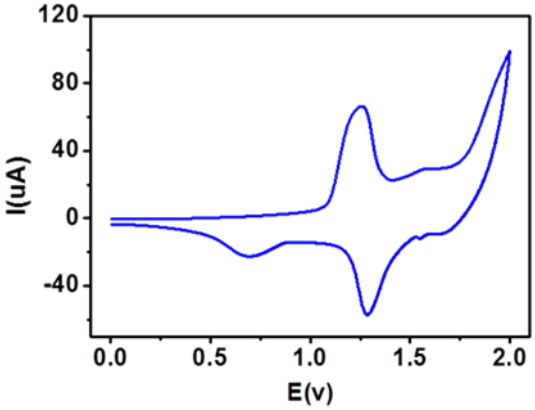

Fig. S2. Cyclic voltammogram of BTBTTBT.