Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information for:
Easily Solution-Processed, High-Performance Microribbon Transistors Based on a 2D Condensed Benzothiophene Derivative

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General. All experiments were performed under an atmosphere of dry argon. Solvents tetrahydrofuran were dried over sodium and distilled before used for reaction. 2-(4',4',5',5'-Tetramethyl-1',3',2'-dioxaborolane)benzo[*b*]thiophene was obtained by lithiated and treated with 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane according to the literature.[1] Other reagents and chemicals were obtained from commercial sources and used without further purification. ^{1}H-NMR spectra were recorded on a Varian 400 MHz spectrometer in deuterated chloroform with tetramethylsilane as an internal reference. All chemical shifts were reported relative to tetramethylsilane (TMS) at 0.0 ppm. GC was performed on a TRACE DSQ and MicroTOF-Q II. Elemental analyses were performed by the elementar vario III. Cyclic voltammeter (CV) was run on a CHI660C electrochemistry station in CH_2Cl_2 solution using tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) as electrolyte at a scan of 100mV/s, by using ITO as working electrode, Pt wire as counter electrode. The **TBTDBT** was deposited onto the ITO electrode by evaporation under vacuum before measured. The UV-vis spectra were obtained on a JΛSCO V-570 UV/vis spectrometer. X-Ray diffraction measurement was performed in reflection mode at 40 kV and 200 mA with Cu Ka radiation using a 2-kW Rigaku D/max-2500 X-ray diffractometer.

Synthesis of 2,3,4,5-tera(benzothieno)thiophene, 3: A mixture of tetrabromothiophene (2.0g, 5mmol), sodium carbonate (17.0g) and 80.0ml distilled water was added to a vacuum three-necked flask. After the $Pd(PPh_3)_4$ (1.2g) was added and degassed again, a toluene solution (120 mL) of **2** (13.0 g, 50 mmol) was added and reflux at 90 ^{o}C for two days. After cooling to ambient temperature, the mixture was washed in water, and the organic phase was dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure, and the residue was purified by flash column chromatography on silica gel using CH_2Cl_2 as eluent, followed with a recrystallization from CH_2Cl_2 to give **3** as yellow solid 0.67 g (22%). MS (Maldi-TOF): m/z 612. ^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ7.84 (t, 8H), 7.79 (s, 4H), 7.39(m, 8H)。

Synthesis of 1,2,3,4,5,6,7,8-tera(benzothieno)dibenzothiophene, TBTDBT, 4: 3 (306 mg, 0.5 mmol) was dissolved in 250 mL super dry CH_2Cl_2, a saturated stream of argon was bubbled into the solution through a steel needle. A solution of 466 mg iron (III) chloride (2.9 mmol) in 5 mL nitromethane was added. After stirred for 2 hour, the reaction was stopped with methanol. The precipitate was filtered off and washed extensively with water and methanol. Repetitive extracted with CHC13 gave 250 mg of the desired product as a yellow powder (82 %,). MS (Maldi-TOF): m/z (%) = 608. ^{1}HNMR (300Hz, 380K, $C_2D_2Cl_4$): δ 8.95 (m, 4H), 8.03 (m, 4H), 7.50 (m, 8H). Elemental analysis calculated for $C_{36}H_{16}S_5$： C, 71.02; H, 2.65; S, 26.33. Found: C, 69.16; H, 2.54; S, 26.44.

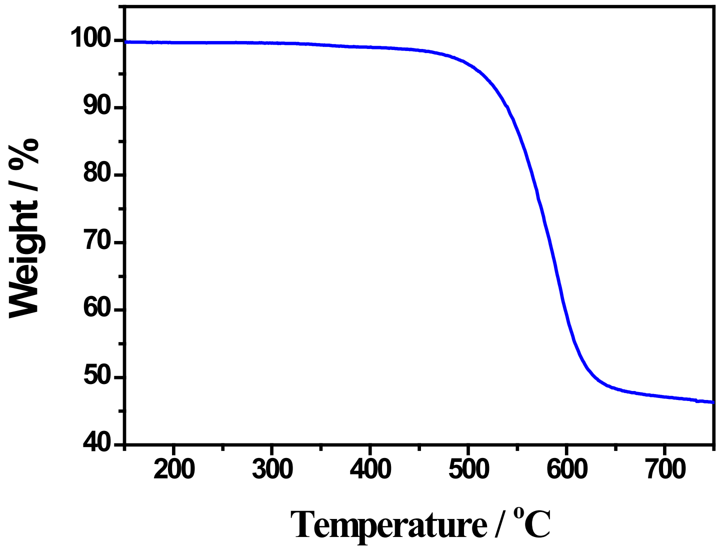

Fig. S1. TGA of the **TBTDBT**

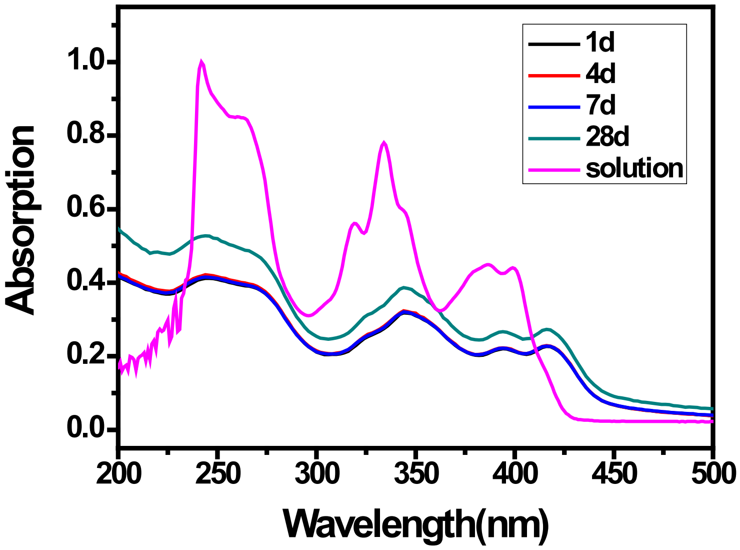

Fig. S2 The absorption spectra of the thin film and solution of **TBTDBT.**

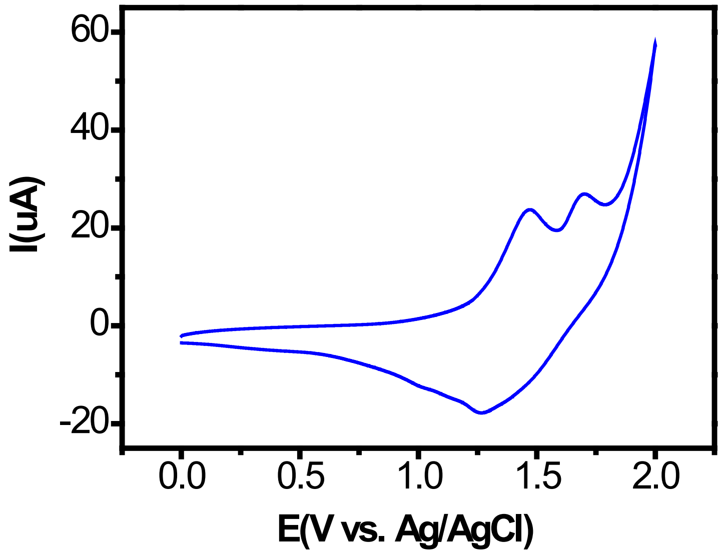

Fig. S3. Cyclic voltammogram of **TBTDBT** in CH_2Cl_2 solution using Ag/AgCl as reference electrode.

Calculation on TBTDBT: the molecular-orbital (MO) calculations of the HOMO and LUMO levels were carried out using the GAUSSIAN03 package.[2] The density functional theory (DFT) calculation and structure optimization of **TBTDBT** were conducted at the B3LYP/6-31+G (d, p) level.

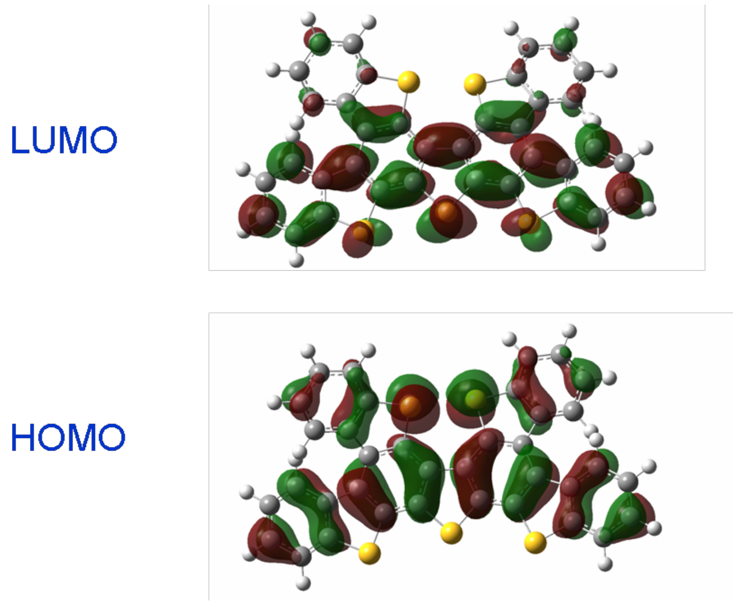

Fig. 4. HOMO and LUMO orbital of **TBTDBT** obtained by using DFT calculations.

Fabrication of OFET devices

Bottom-gate/top contact OFETs were fabricated with conventional techniques. Briefly, a heavily doped n-type Si wafer and a layer of dry oxidized SiO_2 were used as a gate electrode and gate dielectric layer, respectively. The substrate was modified with n-octadecyl-trichlorosilane (OTS) and cleaned in hexene, chloroform and isopropyl alcohol, respectively. **TBTDBT** were dissolved in chlorobenzene, stirring for several hours and filtered. Then the clear solution was drop casted on the OTS modified silicon oxide substrate. The single ctystalline microribbons were obtained after the solvent volatilized. Then the drain-source (D-S) gold contacts were fabricated on the **TBTDBT** single ctystal microribbon by thermal evaporation, using an organic wire as shadow mask. OFET characteristics were measured at room temperature in air by Keithley 4200 SCS and Micromanipulator 6150 probe station. And the field-effect mobility of hole (μ_h) was calculated by fitting a straight line to the plot of the square root of I_DS vs. $\mathrm{V_G}$ (saturation region), according to the expression $I_\mathrm{DS}= (\mathrm{W}/2\mathrm{L})\mu_\mathrm{h}Ci(V_G-V_{th})^2$.

The physical vapor transport microribbons were grown in a horizontal tube furnace, the **TBTDBT** was placed in the ceramic boat at the high-temperature zone of the quartz tube and the SiO_2 wafer was at low-temperature. The furnace temperature was increased to 360 °C and then kept at that temperature for 2h. Finally, the temperature was allowed to descend to room temperature.

Reference

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2. Gaussian 03, Revision C.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J.

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