

Electronic Supplementary Information (ESI)

**Solution-grown unidirectionally oriented crystalline thin films
of a U-shaped thienoacene-based semiconductor
for high-performance organic field-effect transistors**

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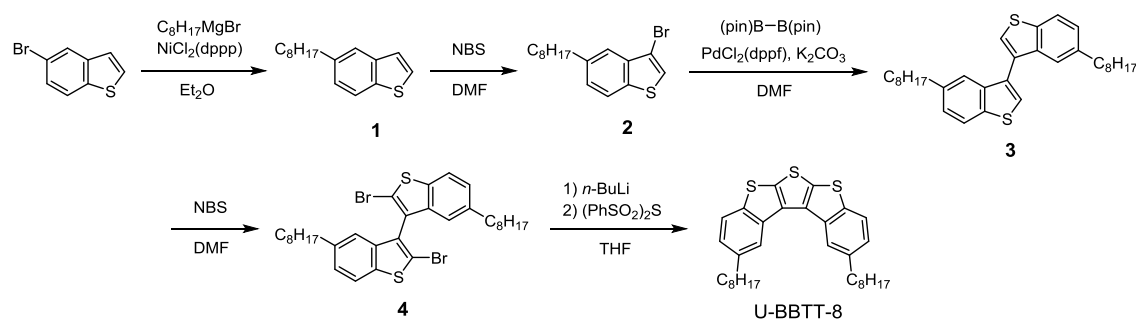
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General Methods. ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance III 400 spectrometer. Chemical shifts of ^1H and ^{13}C NMR signals were quoted to tetramethylsilane ($\delta = 0.00$) and CDCl_3 ($\delta = 77.0$) as internal standards. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectra were collected on a Bruker Daltonics Autoflex III spectrometer using dithranol as the matrix. Elemental analysis was carried out with a Yanaco MT-5 CHN corder. UV-vis absorption spectra were measured with a JASCO V-670Y spectrometer. The HOMO energy levels of materials in thin films were determined using a Riken-Keiki AC-2 ultraviolet photoelectron spectrometer. Differential scanning calorimetry (DSC) was performed using a Hitachi High-Tech Science DSC7000X at a heating rate of $10\text{ }^\circ\text{C min}^{-1}$ under N_2 . Atomic force microscopy (AFM) was performed using a JEOL JSPM-5400 scanning probe microscope with tapping-mode in air. X-ray diffraction (XRD) measurements were carried out using a Rigaku SmartLab. X-ray crystallographic analysis was made on a Rigaku VariMax with a Saturn 724+ system with graphite monochromated $\text{MoK}\alpha$ radiation. Single crystals of U-BBTT-8 were grown by slow diffusion of methanol vapor into its chloroform solution. The structure was solved by the direct method (SIR-2008)¹ and refined by the full-matrix least-square techniques based on F^2 (SHELXL-97).² The density-functional theory (DFT) computations were performed with the Gaussian 09 program package, using the B3LYP functional with the 6-31G(d) basis set.

OFET Device Fabrication and Measurements. For all of the OFET devices, heavily doped n-type Si wafers with a thermally grown 300-nm-thick SiO_2 layer were used as substrates. The SiO_2/Si substrates were pretreated with a piranha solution at $90\text{ }^\circ\text{C}$ for 1 h, and then copiously cleaned by sonication in deionized water, acetone, and isopropanol for 15 min each, and then subjected to UV/ozone treatment for 30 min. Thin films of U-BBTT-8 were then deposited by dip-coating from its 3 g L^{-1} toluene solution at a pulling rate of $2\text{ }\mu\text{m s}^{-1}$ under ambient conditions. As for single-crystal OFETs, the surface of the SiO_2/Si substrates was treated with octyltrichlorosilane (OTS) to reduce charge traps by silanol groups on SiO_2 and facilitate molecular self-organization during the fabrication process, providing superior quality crystals. Single crystals of U-BBTT-8 were grown by drop-casting from its 2 g L^{-1} anisole solution on the OTS-treated SiO_2/Si

substrates. The drop-cast solution was then dried for 12 h in a dry N₂-filled glove box at room temperature. Both thin-film and single-crystal OFET devices were completed by evaporating Au (thickness = 50 nm) through a shadow mask to define the source and drain electrodes with a channel length of 20–100 μm on top of each active layer. The output and transfer characteristics of the OFETs were measured using an Agilent B1500A semiconductor parameter analyzer in air at room temperature. Field-effect mobilities (μ) were calculated in the saturation regime using the following equation: $I_D = (W/2L)\mu C_i(V_G - V_{th})^2$, where I_D is the drain current, W and L are channel width and length, respectively, C_i is the capacitance per unit area of the gate dielectric (11.5 nF cm⁻² for untreated substrates, 11.1 nF cm⁻² for OTS-treated substrates), V_G is the gate voltage, and V_{th} is the threshold voltage.

Synthesis and Characterizations. Commercially available reagents and solvents were used without further purification unless otherwise noted. All of the reactions were performed under N₂ in dry solvents, using standard Schlenk techniques. U-BBTT-8 was prepared according to Scheme S1, by modifying a reported procedure.³



Scheme S1. Synthesis of U-BBTT-8.

5-Octylbenzo[*b*]thiophene (1): To a stirred solution of 5-bromobenzo[*b*]thiophene (10.4 g, 49.0 mmol) and NiCl₂(dppp) (1.26 g, 2.32 mmol) in dry diethyl ether (200 mL) was added dropwise octylmagnesium bromide (2.0 M in diethyl ether, 35.3 mL, 70.5 mmol). The mixture was stirred for 12 h at room temperature. The reaction mixture was poured into a water, and then extracted with hexane. The combined organic layers were washed with water, and dried over anhydrous Na₂SO₄. After filtration and evaporation, the product was purified by silica gel column chromatography (eluent: hexane), and dried

under vacuum to afford **1** as a yellow oil (yield = 10.0 g, 83%). ¹H NMR (400 MHz, CDCl₃): δ 7.77 (d, *J* = 8.4 Hz, 1H), 7.62 (d, *J* = 0.8 Hz, 1H), 7.40 (d, *J* = 5.4 Hz, 1H), 7.27 (dd, *J* = 5.4, 0.8 Hz, 1H), 7.18 (dd, *J* = 8.4, 2.0 Hz, 1H), 2.72 (t, *J* = 7.8 Hz, 2H), 1.70-1.62 (m, 2H), 1.35-1.20 (m, 10H), 0.88 (t, *J* = 6.8 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 139.89, 139.03, 137.11, 126.25, 125.40, 123.59, 122.91, 122.07, 35.91, 31.91, 31.86, 29.52, 29.34, 29.29, 22.68, 14.11. MS (MALDI-TOF): *m/z* 245.95 [*M*]⁺; calcd 246.14.

3-Bromo-5-octylbenzo[*b*]thiophene (2): To a stirred solution of **1** (10.0 g, 40.6 mmol) in dry DMF (100 mL) was added *N*-bromosuccinimide (NBS, 7.51 g, 42.2 mmol) at 0 °C. The mixture was allowed to warm up to room temperature and stirred overnight. The reaction mixture was poured into an aqueous Na₂SO₃, and then extracted with hexane. The combined organic layers were washed with water, and dried over anhydrous Na₂SO₄. After filtration and evaporation, the product was purified by silica gel column chromatography (eluent: hexane), and dried under vacuum to afford **2** as a colorless oil (yield = 10.5 g, 80%). ¹H NMR (400 MHz, CDCl₃): δ 7.75 (d, *J* = 8.4 Hz, 1H), 7.62 (d, *J* = 1.2 Hz, 1H), 7.40 (s, 1H), 7.25 (dd, *J* = 8.4, 1.2 Hz, 2H), 2.76 (t, *J* = 7.8 Hz, 2H), 1.73-1.64 (m, 2H), 1.37-1.20 (m, 10H), 0.88 (t, *J* = 6.8 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 140.14, 137.61, 135.90, 126.43, 123.38, 122.33, 122.22, 107.36, 35.95, 31.88, 31.81, 29.47, 29.33, 29.26, 22.67, 14.10. MS (MALDI-TOF): *m/z* 323.60 [*M*]⁺; calcd 324.05.

5, 5'-Diocetyl-3,3'-bibenzo[*b*]thiophene (3): A mixture of **2** (10.5 g, 32.3 mmol), bis(pinacolato)diboron (4.32 g, 17.0 mmol), PdCl₂(dppf) (0.29 g, 0.36 mmol), and potassium carbonate (13.4 g, 97.2 mmol) in dry DMF (100 mL) was stirred overnight at 80 °C. After cooling to room temperature, the reaction mixture was poured into water, and then extracted with hexane. The combined organic layers were washed with water, and dried over anhydrous Na₂SO₄. After filtration and evaporation, the product was purified by silica gel column chromatography (eluent: hexane), and dried under vacuum to afford **3** as a yellow oil (yield = 6.52 g, 82%). ¹H NMR (400 MHz, DMSO-*d*₆): δ 7.99 (d, *J* = 8.0 Hz, 2H), 7.88 (s, 2H), 7.43 (d, *J* = 1.2 Hz, 2H), 7.25 (dd, *J* = 8.0, 1.2 Hz, 2H), 2.62 (t, *J* = 7.8 Hz, 4H), 1.60-1.50 (m, 4H), 1.30-1.15 (m, 20H), 0.82 (t, *J* = 6.8 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃): δ 139.42, 138.84, 137.60, 131.40, 125.81, 124.77, 122.66, 122.47, 36.07, 32.16, 31.90, 29.50, 29.38, 29.28, 22.67, 14.12. MS (MALDI-TOF): *m/z*

490.06 [M]⁺; calcd 490.27.

2,2'-Dibromo-5, 5'-dioctyl-3,3'-bibenzo[*b*]thiophene (4): To a stirred solution of **3** (5.50 g, 11.2 mmol) in dry DMF (50 mL) was added *N*-bromosuccinimide (NBS, 4.37 g, 24.6 mmol) at 0 °C. The mixture was stirred overnight at 40 °C. The reaction mixture was poured into an aqueous Na₂SO₃, and then extracted with hexane. The combined organic layers were washed with water, and dried over anhydrous Na₂SO₄. After filtration and evaporation, the product was purified by silica gel column chromatography (eluent: hexane/chloroform = 19:1, v/v), and dried under vacuum to afford **4** as a yellow oil (yield = 5.65 g, 78%). ¹H NMR (400 MHz, CDCl₃): δ 7.72 (d, *J* = 8.4 Hz, 2H), 7.22 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.07 (d, *J* = 1.2 Hz, 2H), 2.58 (t, *J* = 7.8 Hz, 4H), 1.55-1.20 (m, 24H), 0.85 (t, *J* = 6.8 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃): δ 140.03, 138.25, 137.13, 130.01, 126.02, 122.48, 121.47, 116.60, 35.87, 31.95, 31.85, 29.42, 29.26, 29.23, 22.64, 14.10. MS (MALDI-TOF): *m/z* 646.00 [M]⁺; calcd 646.09.

U-BBTT-8: To stirred solution of **4** (5.65 g, 8.71 mmol) in dry THF (200 mL) added dropwise *n*-butyllithium (1.6 M in hexane, 11.4 mL, 18.2 mmol) at -78 °C, and the mixture was allowed to react for 1 h at that temperature. Bis(phenylsulfonyl)sulfide (1.13 g, 3.59 mmol) was then added, and the mixture was stirred for 30 min at -78 °C. The mixture was stirred overnight at room temperature. The reaction mixture was poured into a water, and then extracted with chloroform. The combined organic layers were washed with water, and dried over anhydrous Na₂SO₄. After filtration and evaporation, the product was purified by silica gel column chromatography (eluent: hexane), and recrystallized from chloroform to afford U-BBTT-8 as a white solid (yield = 0.70 g, 17%). This compound was further purified by temperature-gradient vacuum sublimation before use. ¹H NMR (DMSO-*d*₆): δ 8.42 (d, *J* = 1.2 Hz, 1H), 8.03 (d, *J* = 8.4 Hz, 2H), 7.34 (dd, *J* = 8.4, 1.2 Hz, 2H), 2.89 (t, *J* = 7.4 Hz, 4H), 1.85-1.75 (m, 4H), 1.45-1.20 (m, 20H), 0.83 (t, *J* = 6.8 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃): δ 140.46, 139.54, 139.41, 134.54, 132.78, 124.92, 123.05, 122.80, 36.24, 31.93, 31.60, 29.64, 29.39, 29.35, 22.68, 14.09. MS (MALDI-TOF): *m/z* 519.95 [M]⁺; calcd 520.23. Anal. Calcd (%) for C₃₂H₄₀S₃: C 73.79, H 7.74; found: C 73.79, H 7.84.

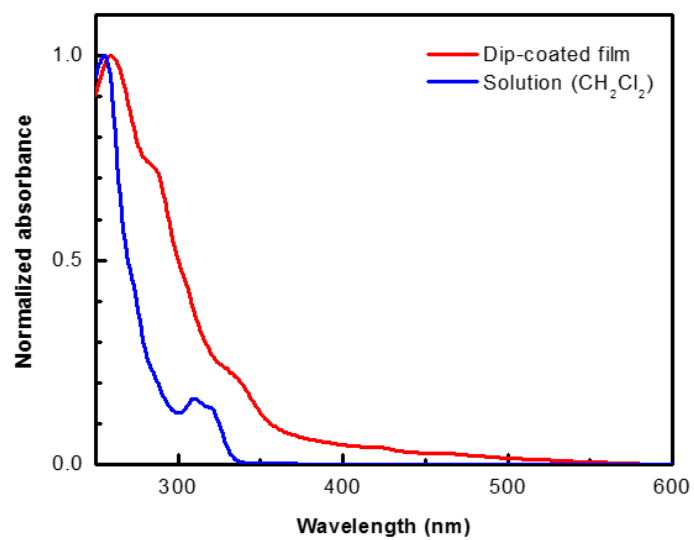


Fig. S1 UV-vis absorption spectra of U-BBTT-8 in CH_2Cl_2 solution and in a thin film.

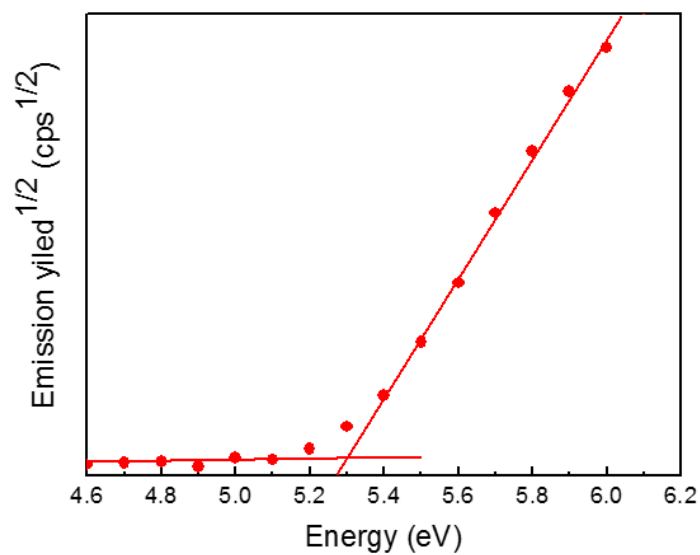


Fig. S2 Photoelectron yield spectrum of U-BBTT-8 in a thin film.

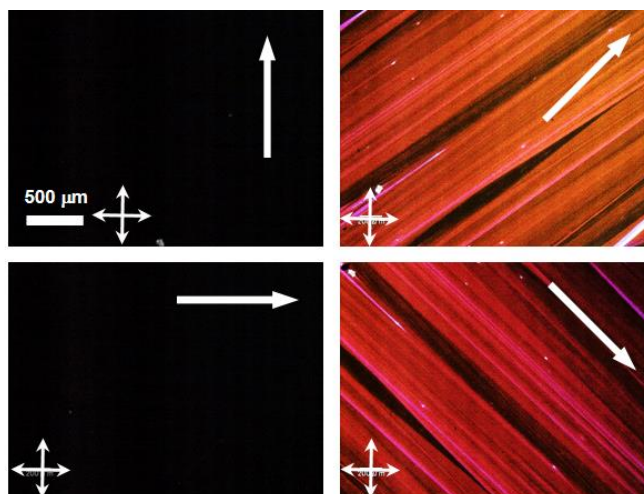


Fig. S3 Polarizing optical microscopy (POM) images of a dip-coated thin film of U-BBTT-8 under the crossed Nicols condition. The crossed arrows indicate the direction of crossed polarizers, and the white arrow denotes the sample pulling direction. Rotation of the sample by 45° produces periodic bright and dark images showing unidirectional orientation along the sample pulling direction.

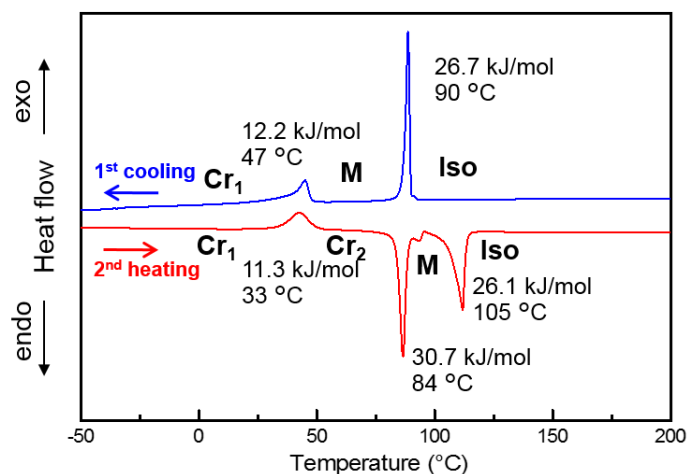


Fig. S4 DSC thermogram of U-BBTT-8 at a scanning rate of $10\text{ }^\circ\text{C min}^{-1}$. Abbreviations: Cr₁, Cr₂, crystalline phases; M, liquid-crystalline mesophase; Iso, isotropic phase. Upon heating, an exothermic peak corresponding to recrystallization from the Cr₁ to Cr₂ phases was detected at $33\text{ }^\circ\text{C}$. U-BBTT-8 then melted at $84\text{ }^\circ\text{C}$ to form liquid-crystalline mesophase (M), which was retained up to $105\text{ }^\circ\text{C}$ before isotropization. Upon cooling, the M phase directly transformed into the Cr₁ phase at $47\text{ }^\circ\text{C}$.

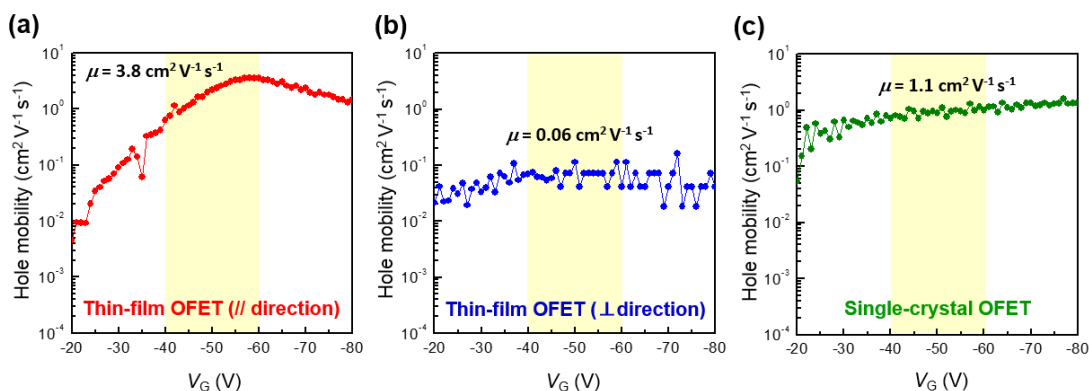


Fig. S5 Mobility versus gate voltage (μ - V_G) plots for (a,b) the representative thin-film OFET (see Fig. 3d) and (c) the single-crystal OFET (see Fig. 4b).

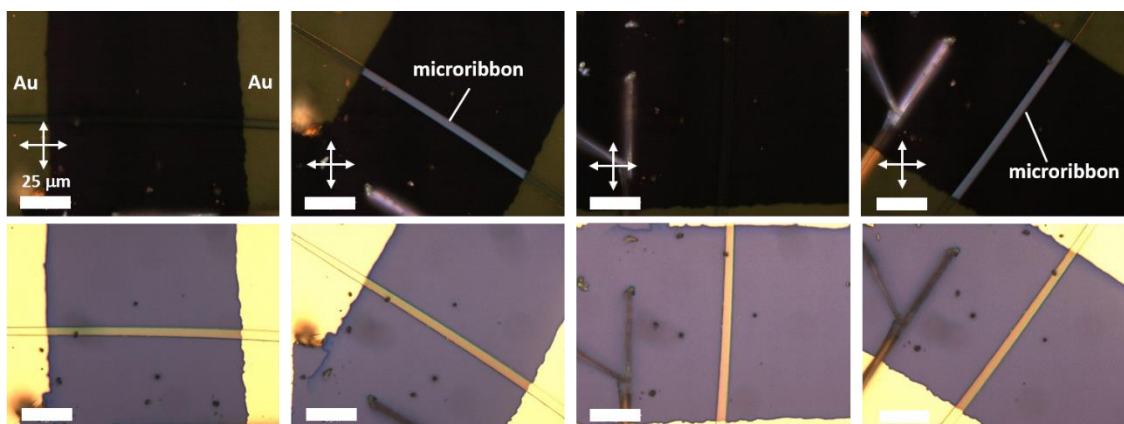


Fig. S6 POM images (top panels) and corresponding optical microscopy images (bottom panels) for the representative single-crystal OFET based on a U-BBTT-8 microribbon under the crossed Nicols condition. The crossed arrows indicate the direction of crossed polarizers. Rotation of the sample by 45° produces periodic bright and dark images.

References

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