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Electronic Supplementary Information (ESI)

S-Shaped thienoacene semiconductor forming unique cruciform lamellar packing via 2D interaction network of π-stacking and chalcogen bonding

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1. Methods

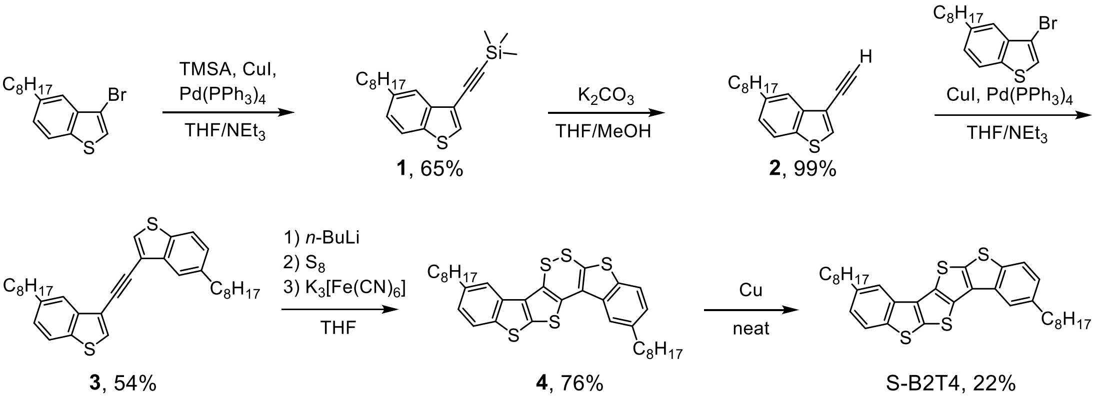
Nuclear magnetic resonance (NMR) spectra were recorded on an Avance III 400 spectrometer (Bruker). Chemical shifts were referenced to tetramethylsilane ($\delta = 0.00$) for ^{1}H NMR, and $CDCl_3$ ($\delta = 77.0$) for ^{13}C NMR as internal standards. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectra were collected on an Autoflex III spectrometer (Bruker Daltonics) using dithranol as the matrix. Elemental analysis was carried out with an MT-5 CHN corder (Yanaco). UV–vis absorption spectra were measured using a V-670Y spectrometer (Jasco). Cyclic voltammetry (CV) was performed using a CHI 612E electrochemical analyzer (ALS) and a three-electrode cell equipped with Pt working and counter electrodes and an $Ag/AgNO_3$ reference electrode. Tetrabutyl ammonium perchlorate (n-Bu_4NClO_4) was used as a supporting electrolyte with a concentration of 0.1 M. The redox potentials were calibrated with ferrocene as an internal standard. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed on a TG/DTA7300 and DSC7000X systems (Hitachi High-Tech Science), respectively, at a scanning rate of 10 °C min^{-1} under N_2. Density functional theory (DFT) computations were performed with the Gaussian 16 program package, using the B3LYP functional with the 6-31G(d) basis set. Out-of-plane XRD patterns of the thin films were recorded using a SmartLab diffractometer (Rigaku) with Cu$K\alpha$ radiation ($\lambda = 1.541$ Å). Atomic force microscopy (AFM) measurements were carried out using a Dimension Icon scanning probe microscope (Bruker) in tapping mode in air. The sample were prepared on Si/SiO_2 substrates in the same manner as actual devices. X-ray crystallographic analysis was performed on a VariMax with a Saturn70 system (Rigaku) with multi-layer mirror monochromated Mo$K\alpha$ radiation. The structures were solved by direct method (SHELXT)[1] and refined by the full-matric least-squares on F^2 (SHELXL).[2] All non-hydrogen atoms were refined with anisotropic displacement parameters, whereas the hydrogen atoms were refined using AFIX instructions. The crystallographic data of S-B2T4 has been deposited at the Cambridge Crystallographic Data Centre as supplementary publication (CCDC 2103144).

2. OFET device fabrication and measurements

All OFET devices were fabricated in a top-contact, bottom-gate configuration on heavily doped n-type Si wafer with a 200 nm-thick SiO_2 dielectric layer. The Si/SiO_2 substrates were cleaned by sonication in acetone and isopropanol for 10 min each and exposed to isopropanol vapor for 2 min, and then subjected to UV/O_3 treatment for 20 min. Thin films were then deposited by dip-coating from the solutions (5 g L^{-1}) at a constant pulling rate (4 µm s^{-1}) using a DT-0001-S2 dip-coater (SDI) under N_2. Thin-film 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 50–60 µm on top of each active layer. The transfer and output characteristics of the OFETs were measured using a B2902A source measure unit (Keysight Technologies) 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 the channel width and length, respectively, C_i is the capacitance per unit area of the gate dielectric (17.7 nF cm^{-2} for Si/SiO_2 substrates), V_G is the gate voltage, and V_{th} is the threshold voltage.

3. Synthesis and characterization

All reagents and solvents were purchased from Sigma-Aldrich, Tokyo Chemical Industry (TCI), or Fujifilm Wako Pure Chemical Corp., and were used as received unless otherwise noted. All reactions were performed under N_2 in dry solvents, using standard Schlenk techniques. 3-Bromo-5-octylbenzo[*b*]thiophene was prepared according to the previous report.[3]



Scheme S1 Synthetic route for S-B2T4.

Compound 1: A mixture of 3-bromo-5-octylbenzo[*b*]thiophene (10.4 g, 32.0 mmol), trimethylsilylacetylene (4.83 g, 49.2 mmol), $Pd(PPh_3)_4$ (0.75 g, 0.65 mmol), copper(I) iodide (0.12 g, 0.64 mmol) in dry THF (100 mL) and triethylamine (20 mL) was stirred for 2 days at 80 °C. After cooling to room temperature, the reaction mixture was added into water, and the product was extracted with hexane. The combined organic layer was washed with water and dried over anhydrous Na_2SO_4. After filtration and evaporation, the product was purified by silica gel column chromatography (eluent: hexane) to afford **1** as an orange oil (yield = 7.16 g, 65%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, J = 8.0 Hz, 1H), 7.69 (d, J = 1.2 Hz, 1H), 7.61 (s, 1H), 7.23 (dd, J = 8.0, 1.6 Hz, 1H), 2.76 (t, J = 7.8 Hz, 2H), 1.74–1.63 (m, 2H), 1.40–1.23 (m, 10H), 0.88 (t, J = 7.0 Hz, 3H), 0.31 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.73, 139.44, 136.13, 130.82, 126.19, 122.27, 122.14, 98.67, 96.90, 35.91, 31.90, 31.73, 29.50, 29.32, 29.27, 22.68, 14.11, 0.12. MS (MALDI-TOF): *m/z* calcd 342.18 $[M]^+$; found 341.90.

Compound 2: A mixture of **1** (5.19 g, 15.1 mmol) and K_2CO_3 (3.12 g, 22.6 mmol) in dry THF (50 mL) and methanol (30 mL) was stirred for 3 h at room temperature. The reaction was quenched with an aqueous NH_4Cl, and the product was extracted with hexane. The combined organic layer was washed with water and dried over anhydrous Na_2SO_4. After filtration and evaporation, the product was purified by silica gel column chromatography (eluent: hexane) to afford **2** as a colorless oil (yield = 4.04 g, 99%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.75–7.73 (m, 2H), 7.66 (s, 1H), 7.24 (dd, J = 8.4, 1.6 Hz, 1H), 3.30 (s, 1H), 2.75 (t, J = 7.8 Hz, 2H), 1.72–1.64 (m, 2H), 1.37–1.27 (m, 10H), 0.88 (t, J = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 139.92, 139.44, 136.15, 131.44, 126.29, 122.19, 116.97, 79.57, 77.68, 35.95, 31.88, 31.85, 29.48, 29.35, 29.26, 22.66, 14.09. (one carbon peak was not recognizable because of overlapping). MS (MALDI-TOF): *m/z* calcd 270.14 $[M]^+$; found 269.83.

Compound 3: A mixture of **2** (3.89 g, 14.4 mmol), 3-bromo-5-octylbenzo[*b*]thiophene (3.75 g, 11.5 mmol), $Pd(PPh_3)_4$ (0.21 g, 0.18 mmol), copper(I) iodide (0.046 g, 0.24 mmol) in dry THF (40 mL) and triethylamine (8 mL) was stirred overnight at 80 °C. After cooling to room temperature, the reaction mixture was added into water, and the product was extracted with hexane. The combined organic layer was washed with water and dried over anhydrous Na_2SO_4. After filtration and evaporation, the product was purified by silica gel column chromatography (eluent: hexane) and recycling preparative gel permeation chromatography (GPC; eluent: chloroform) to afford **3** as an orange solid (yield = 3.20 g, 54%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, J = 1.2 Hz, 2H), 7.79 (d, J = 8.4 Hz, 2H), 7.73 (s, 2H), 7.28 (dd, J = 8.4, 1.6 Hz, 2H), 2.79 (t, J = 7.8 Hz, 4H), 1.75–1.67 (m, 4H), 1.37–1.25 (m, 20H), 0.86 (t, J = 7.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.96, 139.45, 136.34, 130.08, 126.32, 122.37, 122.34, 118.02, 85.47, 36.09, 31.96, 31.89, 29.53, 29.42, 29.29, 22.65, 14.07. MS (MALDI-TOF): *m/z* calcd 514.27 $[M]^+$; found 514.33.

Compound 4: To a stirred solution of **3** (3.60 g, 7.00 mmol) in dry THF (140 mL) was added dropwise *n*-butyllithium (1.57 M in hexane, 9.8 mL, 15.4 mmol) at −78 °C, and the mixture was allowed to react for 1 h at this temperature. After the addition of sulfur powder (0.68 g, 21 mmol), the mixture was kept at the same temperature for 10 min and then allowed to warm up to room temperature and stirred for 2 h. An aqueous NaOH (1 M, 100 mL) and potassium ferricyanide(III) (9.23 g, 28.0 mmol) was added and the mixture was further stirred for 1 h. The formed precipitation was corrected and dried under vacuum to afford **4** as an orange solid (yield = 3.22 g, 76%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 (br, 2H), 7.18 (d, J = 8.4 Hz, 2H), 6.94 (dd, J = 8.2, 1.4 Hz, 2H), 2.60 (t, J = 7.8 Hz, 4H), 1.68–1.64 (m, 4H), 1.38–1.29 (m, 20H), 0.89 (t, J = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.58, 139.06, 137.75, 126.89, 123.34, 122.24, 120.88, 90.31, 67.97, 35.92, 31.97, 31.07, 29.67, 29.41, 25.63, 22.72, 14.12. MS (MALDI-TOF): *m/z* calcd 608.17 $[M]^+$; found 608.27.

S-B2T4: A mixture of **4** (0.61 g, 1.0 mmol) and copper nanopowder (0.25 g, 4.0 mmol) was reacted at 250 °C for 15 min. After cooling to room temperature, the product was dissolved in chloroform and filtered through a celite pad. After evaporation, the crude product was purified by a silica gel column chromatography (eluent: hexane) and recrystallization from chloroform/methanol to afford S-B2T4 as a white solid (yield = 0.13 g, 22%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.78 (d, J = 8.4 Hz, 2H), 7.75 (d, J = 1.2 Hz, 2H), 7.25 (dd, J = 8.0, 1.2 Hz, 2H), 2.83 (t, J = 7.8 Hz, 4H), 1.78–1.71 (m, 4H), 1.41–

1.25 (m, 20H), 0.89 (t, J = 7.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.63 (*C*), 140.08 (*C*), 138.17 (*C*), 133.31 (*C*), 132.02 (*C*), 131.34 (*C*), 125.35 (*CH*), 122.89 (*CH*), 121.12 (*CH*), 36.02 (CH_2), 31.91 (CH_2), 31.90 (CH_2), 29.53 (CH_2), 29.38 (CH_2), 29.30 (CH_2), 22.68 (CH_2), 14.10 (CH_3). MS (MALDI-TOF): *m/z* calcd 576.20 $[M]^+$; found 576.16. Anal calcd (%) for $C_{34}H_{40}S_4$: C 70.78, H 6.99; found C 70.76, H 6.90.

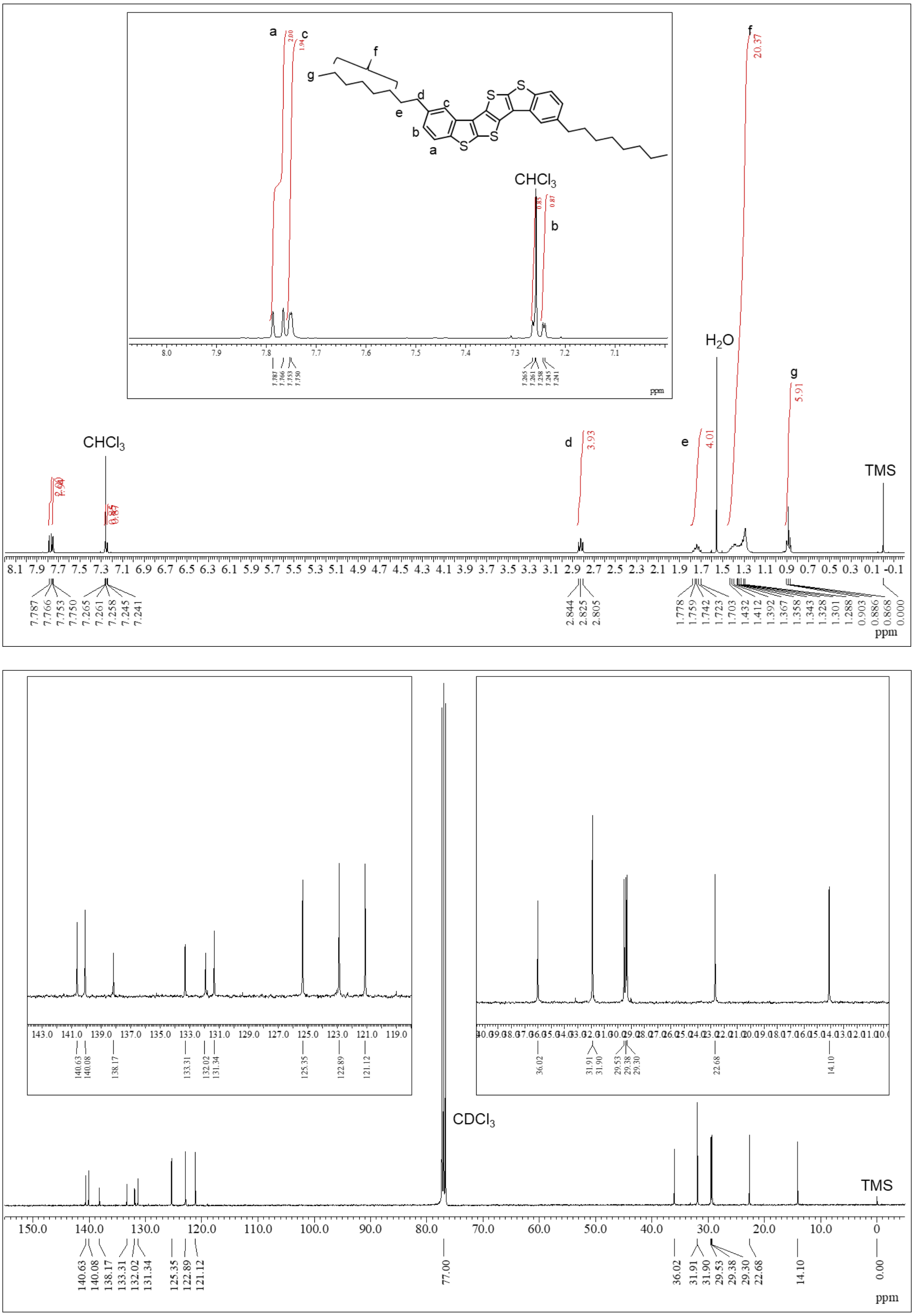


Fig. S1 ^{1}H and ^{13}C NMR spectra of S-B2T4 in CDCl$_3$.

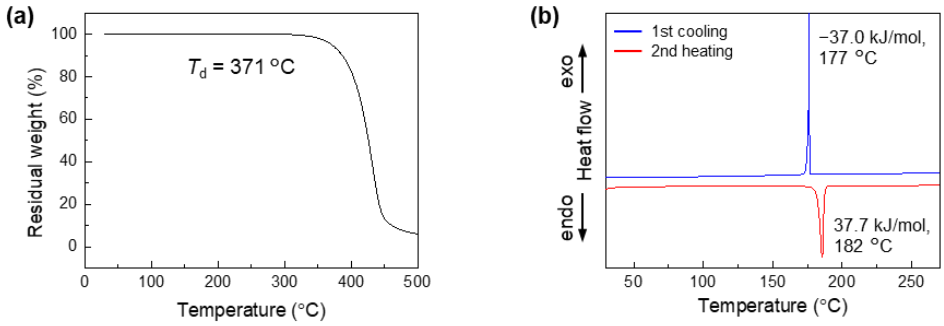


Fig. S2 (a) TGA curve and (b) DSC thermogram at a scanning rate of 10 °C min^{-1} under N_2.

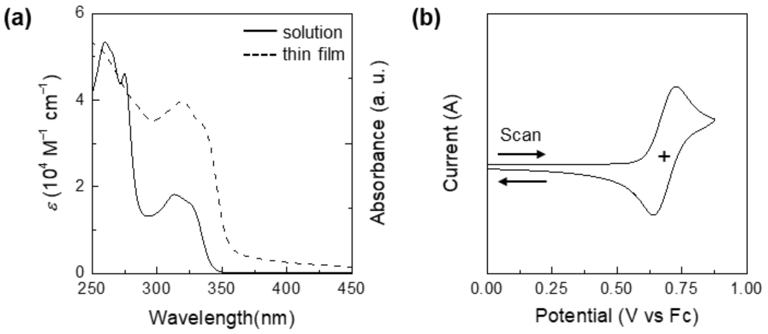


Fig. S3 (a) UV–vis absorption spectra of S-B2T4 in dichloromethane solution (10^{-5} M) and drop-casted thin film. (b) Cyclic voltammogram of S-B2T4 measured in dichloromethane solution (10^{-3} M).

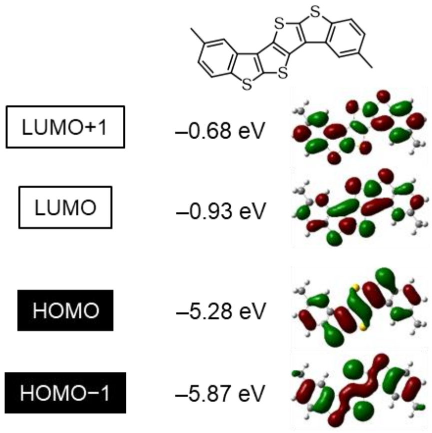


Fig. S4 Energy-level diagram and pictorial frontier molecualr orbitals for S-B2T4 calculated at the B3LYP/6-31G(d) level. The octyl chains are replaced with methyl groups for computational simplicity.

Table S1 Crystallography data for S-B2T4

	S-B2T4
molecular formula	$C_{34}H_{40}S_4$
M [g/mol]	576.934
crystal system	monoclinic
T [K]	113
λ [Å]	0.71073
space group	$C2/c$
a [Å]	15.1351(19)
b [Å]	4.7828(9)
c [Å]	41.376(7)
α [°]	90
β [°]	100.234(13)
γ [°]	90
V [Å^3]	2947.5(8)
Z	4
D_{calcd} [g/cm^3]	1.300
F(000)	1232
no. reflections collected	19692
no. Independent reflections	3377
GOF on F^2	1.175
Final R indices [I>2σ(I)]	R_1 = 0.1378 wR_2 = 0.3679

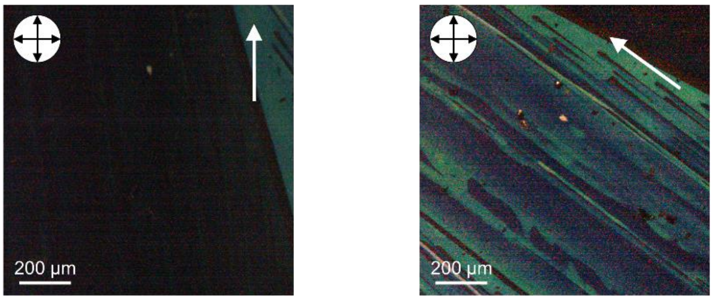


Fig. S5 Polarized optical microscopy (POM) images of a dip-coated thin film of S-B2T4 under the crossed Nicols condition. The crossed arrows indicate the direction of crossed polarizers, and the white arrows denote the sample pulling direction.

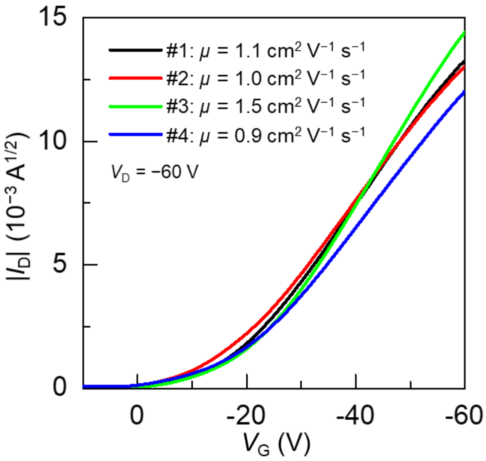


Fig. S6 Transfer characteristics of S-B2T4-based thin-film OFETs. #1 and #2 have been presented in Fig. 5 as representative devices.

Table S2 Thin-film OFET characteristics of S-B2T4[a]

μ_{max}[b] [cm^2 V^{-1} s^{-1}]	μ_{avg}[c] [cm^2 V^{-1} s^{-1}]	V_{th}[d] [V]	$I_{\mathrm{on}}/I_{\mathrm{off}}$[e]
1.5	1.1	−17	1×10^5

[a] OFET parameters along parallel and perpendicular direction were treated together without distinction because of isotropic device performance. [b] Maximum field-effect hole mobility. [c] Average hole mobility obtained with four individual devices. [d] Threshold voltage (on average) determined by extrapolating $|I_D|^{1/2}$ versus V_G plots to $I_D = 0$ A. [e] On/off current ratio (on average) determined from the I_D values at $V_G = -60$ V (I_{on}) and 0 V (I_{off}).

References

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2. G. M. Sheldrick, *Acta Cryst. C*, 2015, **71**, 3–8.
3. T. Mori, T. Oyama, H. Komiyama and T. Yasuda, *J. Mater. Chem. C*, 2017, **5**, 5872–5876.