Dithienobenzobis(thiadiazole) Based Organic Semiconductors with Low LUMO Levels and Narrow Energy Gaps

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General.

Cyclic voltammograms (CVs) were recorded on a HOKUTODENNKO HZ-5000 Automatic Polarization System at 100 °C. Terabutylammonium hexafluorophosphate $Bu_4N\ PF_6$ was used as supporting electrolyte (0.1 M in benzonitrile). The Pt disc and Pt wire were used as the work and counter electrodes. Ag was used as a reference electrode. Thin film UV–vis–NIR spectra were recorded on a SHIMADZU UV-3100. Thin films were deposited on a quartz plates (ca.100 nm) with vacuum evaporation. Ionization potential measurements in thin films were carried out by photoelectron spectroscopy in air with RIKEN KEIKI AC–3. Scanning electron microscopy (SEM) was measured by SHIMADZU SuperScan–550. Atomic force microscopy (AFM) was measured by SII NanoTechnology SPA400 with DFM mode (scan with tapping). Because compounds **2** and **3** did not dissolve in common organic solvents, NMR spectra of these compounds cannot be measured. Elemental analyses and EIMS spectra were performed at Tokyo Institute of Technology, Chemical Resources Laboratory.

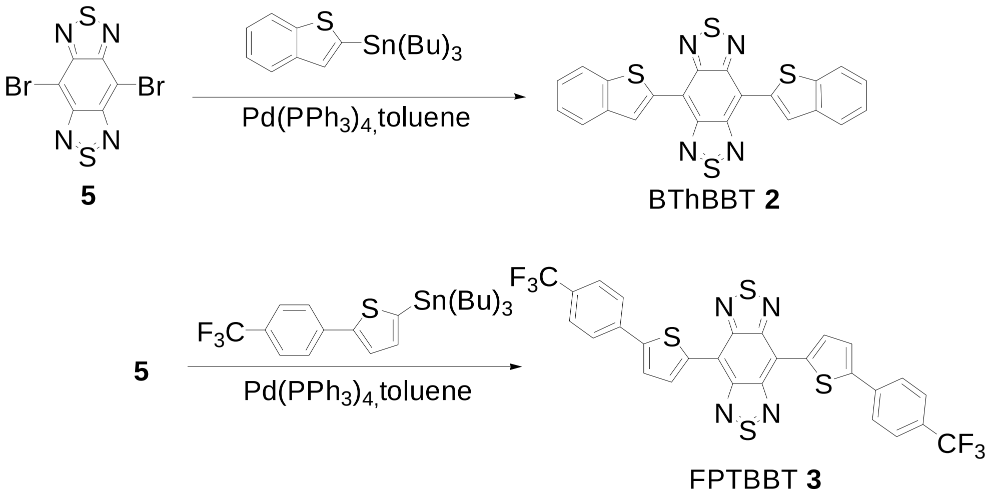
Materials.

Tributyl [5–(4–trifluoromethylphenyl)thiophen-2-yl]stannane (**6**), ThBBT **1**, benzo[b]thiophen-2–yl–tributyl-stannane (**7**), and 4,10–dibromobenzo(bisthiadiazole) (**5**) were prepared according to reported methods. [S1] Toluene was distilled with CaH under argon. Benzonitrile was distilled with CaH under a reduce pressure.

ThBBT (1). 1 was prepared according to a reported method.[S2]
Blue solid. ^1H NMR (400 MHz, $CDCl_3$): 9.03(d), 7.71(d), 7.35(t). Mp: 316 °C (dec.) (DSC). Elemental analysis: Calcd. for $C_{14}H_6N_4S_4$: C, 46.91; H, 1.69; N, 15.63; S, 35.78. Found: C, 47.18; H, 1.45; N, 15.67; S, 36.08

BThBBT (2). 4,10–Dibromobenzobis(thiadiazole) (254 mg, 0.721 mmol), and $Pd(PPh_3)_4$ (51 mg) were placed in a 50 ml 2-neck round bottom flask. Toluene (30 ml) and **7** (860 mg, 2.03 mmol) were added and refluxed for 23 h. After cooling, the resulting solid was filtered off and well washed with hexane and MeOH. The collected green solid was well dried at 100 °C under vacuum. Purification was carried out by twice sublimation. Yield: 112 mg, 34%, blue-black block crystal. Mp: 376 °C (DSC). *m/z* (EIMS): 458. Elemental analysis: Calcd. for $C_{22}H_{10}N_4S_4$: C, 57.62; H, 2.20; N, 12.22. Found: C, 57.50; H, 2.27; N, 12.15.

FPTBBT (3). 4,10–Dibromobenzobis(thiadiazole) (254 mg, 0.721 mmol), $Pd(PPh_3)_4$ (60 mg) were placed in a 50 ml 2-neck round bottom flask. Toluene (30 ml) and **5** (1.05 g 2.02 mmol) were added and refluxed for 72 h. After cooling, the solvent was removed by rotary evaporator and added a large amount of MeOH. The resulting solid was filtered off and well washed with hexane and MeOH. The collected green solid was well dried at 100 °C under vacuum and purified by twice sublimation. Yield: 150 mg, 32%, green solid. Mp: 422 °C (dec.) (DSC). *m/z* (EIMS): 646. Elemental analysis: Calcd. for $C_{28}H_{12}F_6N_4S_4$: C, 52.00; H, 1.87; F, 17.63; N, 8.66; S, 19.83. Found: C, 51.82; H, 1.58; F, 17.50; N, 8.64; S, 19.91.



Scheme 2, Synthesis of **2** and **3**.

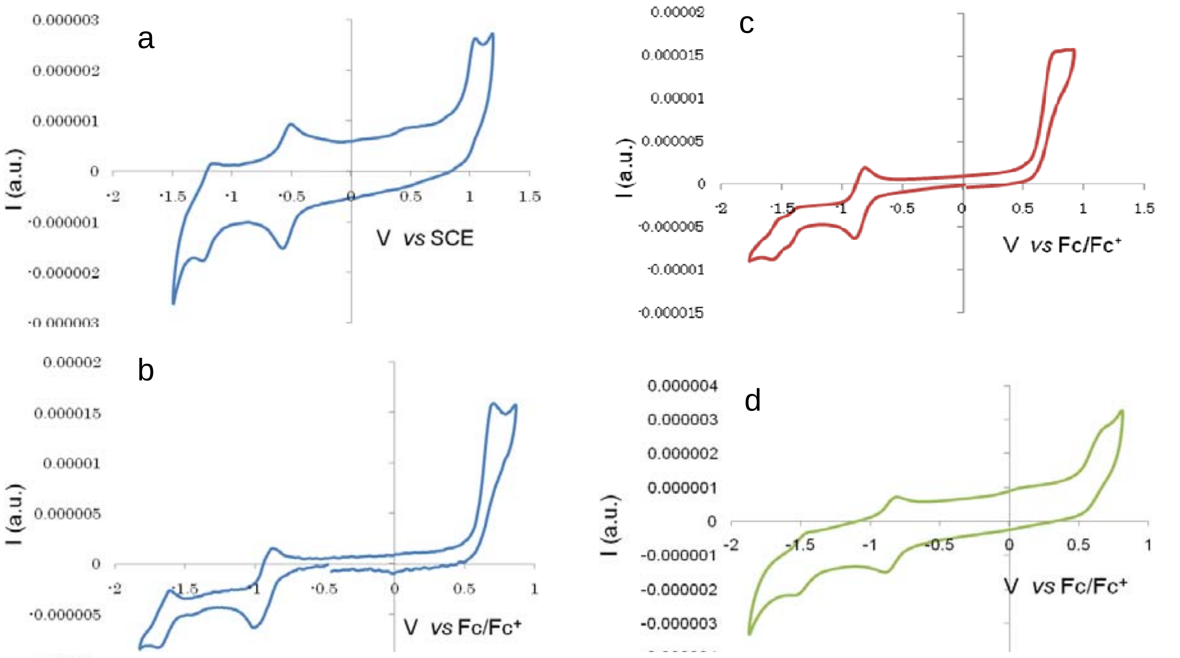


Figure S1. a; Cyclic voltammograms of ThBBT **1** (r.t measured with SCE reference electrode), b; ThBBT **1** (100 °C measured with Ag reference electrode), c; BThBBT **2** (100 °C measured with Ag reference electrode), and d; FPTBBT **3** (100 °C measured with Ag reference electrode) in PhCN with 0.1 M $(Bu)_4NPF_6$.

Because the Fc/Fc$^+$ (4.8 eV) coupling was unstable at 100 ^{o}C, the first reduction coupling of ThBBT (3.86 eV) was used as secondary internal standard.

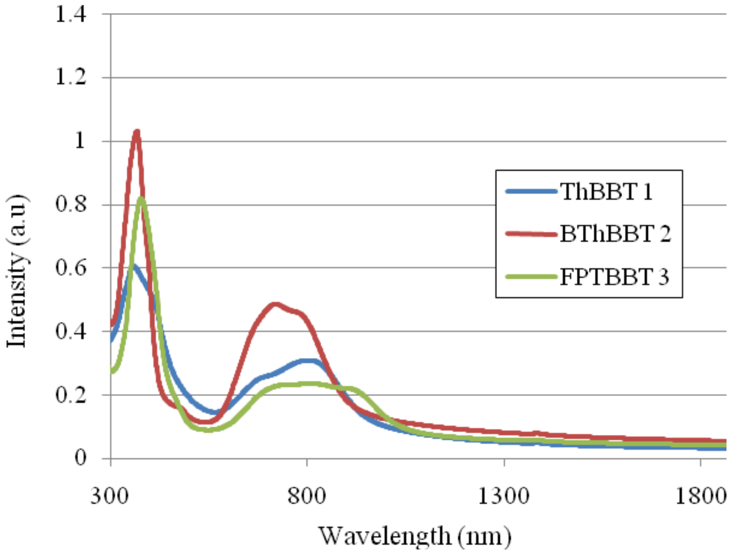


Figure S2. Thin film absorption spectra of ThBBT **1**, BThBBT **2**, and FPTBBT **3**.

Table S1, absorption maxima and redox potentials for **1**–**3** and **4**.

Compd.	Solution^a λ_{max}(nm)	Thin–film^b λ_{max}(nm)	$E^{1/2}_{red1}$ (V)^c	E_{ox1} (V)^c
ThBBT 1	334, 701	360, 806	-0.94	+0.69
BthBBT 2	354, 721	368, 720	-0.86	+0.78
FPTBBT 3	——	378, 810	-0.85	+0.69
FPTBTD 4	348, 480	347, 475	-1.59	+0.98

^{a}Measured with CH_2Cl_2 solution. ^{b}100 nm thickness. ^{c}0.1M Bu_4NPF_6 in PhCN solution. Pt disc, Pt wire were used as working and counter electrode. Ag wire was used as petro-reference electorode (V vs Fc/Fc$^+$). The redox potentials were measured at 100 ^{o}C.

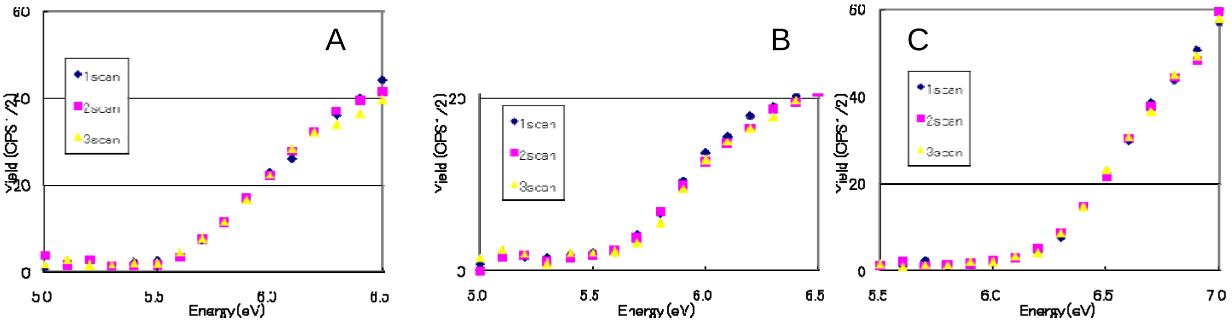


Figure S3. Ionization potential measurements for ThBBT **1** (A), BThBBT **2** (B), and FPTBBT **3** (C).

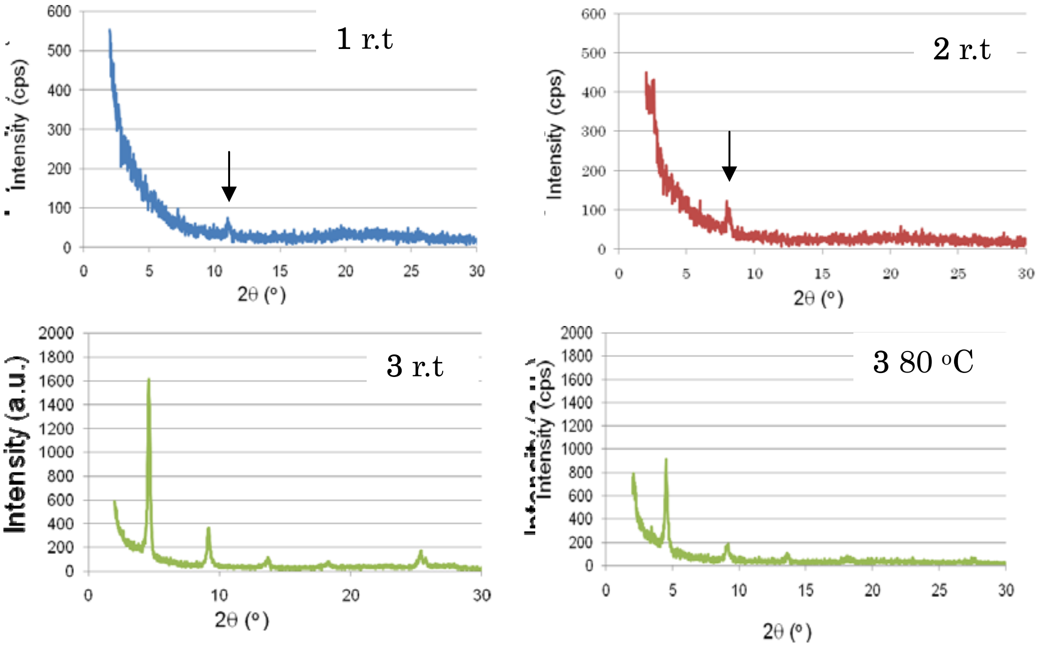


Figure S4. XRD diffraction patterns for **1**–**3** by using HMDS treated substrates.

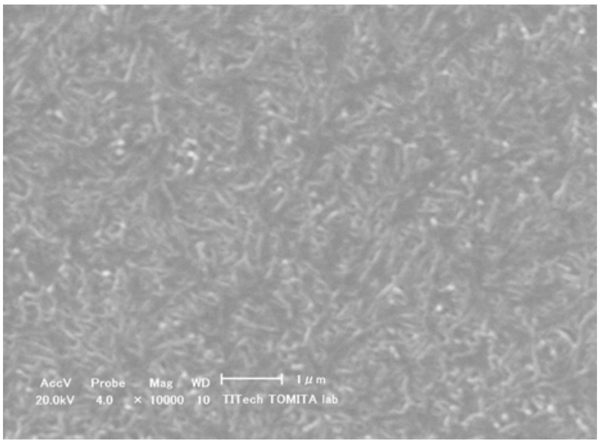


Figure S5. SEM image of BThBBT **2** film (deposited on HMDS treated Si/SiO_2 substrate at r.t).

Top contact devices.

Top contact OFETs were constructed on n^{++}silicon wafers covered with 200 nm–thick thermally grown SiO_2 using as a gate dielectric layer. Organic semiconductors (ca. 50 nm) were deposited by vacuum evaporation. Then the gold source and drain electrodes were deposited by vacuum evaporation through a shadow mask, W/L is 1000 / 50 μm.

Under vacuum, FET characteristics measurements were carried out at room temperature by Hewlett–Packard 4140A and 4140B models. After measurements in vacuum, the FET devices were stored in a laboratory air. Then, to investigate the air stability of device, FET measurements were carried out in a laboratory air.

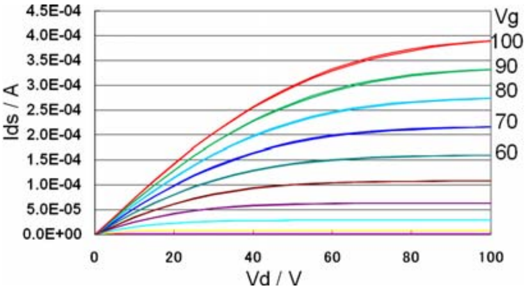


Figure S6. Output curve for **3** (top–contact device in vacuum).

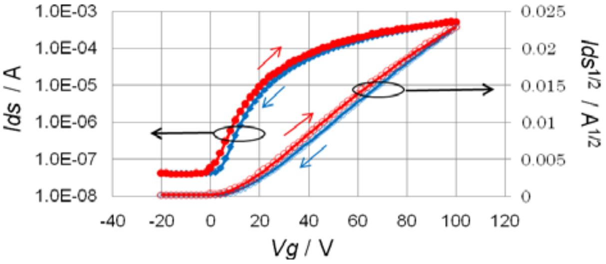


Figure S7. Transfer curves of **3** (top–contact device, measured in vacuum, highest mobility was to be 0.44 cm^2/Vs).

Table S2. Air stability of device **3** (top–contact device).

Day	μ cm^2/Vs	I_{on}/I_{off}	*Vth* V
Vacuum	0.29	4.7×10^{-3}	10.2
0	0.21	3.6×10^{-4}	8.7
3	0.22	4.7×10^{-5}	10.7
5	0.20	3.5×10^{-5}	10.7
11	0.21	6.5×10^{-5}	17.1
20	0.19	3.1×10^{-5}	16.2
30	0.16	8.0×10^{-4}	16.0
41	0.15	5.5×10^{-4}	18.0
50	0.16	1.5×10^{-5}	19.3

W/L = 1000/50 μm. Stored and measured in air.

Bottom contact devices.

Bottom contact OFETs were constructed on n^{++}silicon wafers covered with 300 nm–thick thermally grown SiO$_2$ using as a gate dielectric layer. Interdigitate Cr (10 nm)/Au (20 nm) of source and drain electrodes were placed on SiO$_2$ whose channel length(*L*) and width(*W*) were 25 μm and 294 mm, respectively.

Organic semiconductors were deposited by vacuum evaporation at a rate of 0.2–0.3 Ås^{-1} (ca. 50 nm) for **2** and **3**, and 0.8–1.0 Ås^{-1} (ca. 80 nm) for **1** under a pressure of 10^{-5} Pa. Under vacuum, FET characteristics measurements were carried out at room temperature by using a Keithlly 2400 source meter and Keithlly 6487 picoammeter. After measurement in vacuum, the FET devices were stored in a laboratory air. Then, to investigate air stability, FET measurements were carried out in a laboratory air.

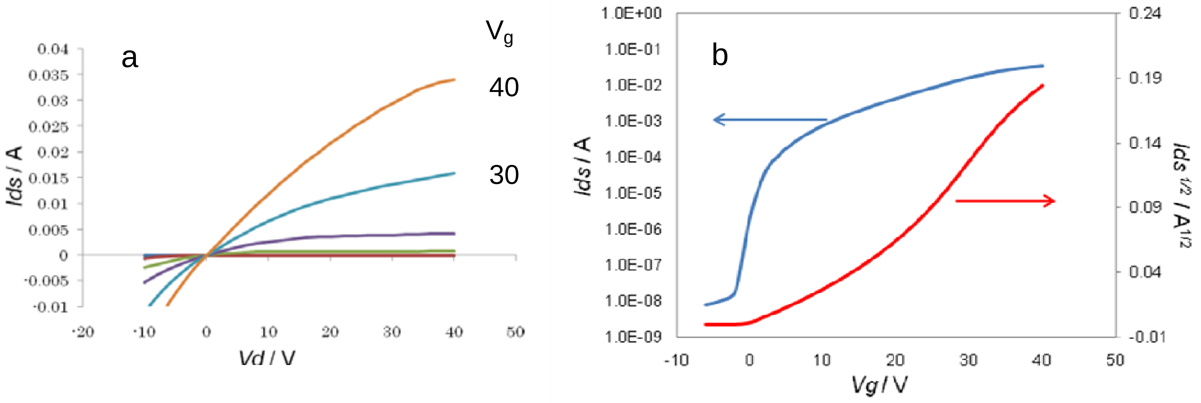


Figure8. Output (a) and transfer (b) plots of **3** at T$_{sub}$=130 °C (bottom–contact device).

Table S3, FET Characteristics of FPTBBT **3** (BC).

Device no.	T_{sub}	μ_e (cm^2/Vs)	I_{on}/I_{off}[a]	Vth
1	r.t	0.341	384, (1.2x10^5)	16.4
2	r.t	0.177	3.4x10^3, (2.1x10^4)	11.2
3	r.t	0.209	1.7x10^3, (1.7x10^4)	14.5
4	r.t	0.347	3.2x10^4, (9.1x10^4)	16.4
5	r.t	0.405	161, (5.3x10^4)	5.6
7	80 °C	0.305	6.4x10^5, (6.4x10^5)	17.2
8	80 °C	0.342	7.5x10^3, (3.5x10^4)	14.2
9	130 °C	0.774	2.6x10^3, (6.3x10^3)	15.4
10	130 °C	0.615	9.3x10^3, (6.5x10^6)	9.2
11	130 °C	0.716	2.2x10^4, (5.3x10^6)	11.2
12	130 °C	0.767	1.6x10^4, (4.6x10^6)	12.4

Measured at r.t in vacuum (10^{-5} Pa). W/L = 294 mm/25 µm. [a]Higest I_{on}/I_{off} ratios obtained using lowest I_{off} values are shown in the parentheses.

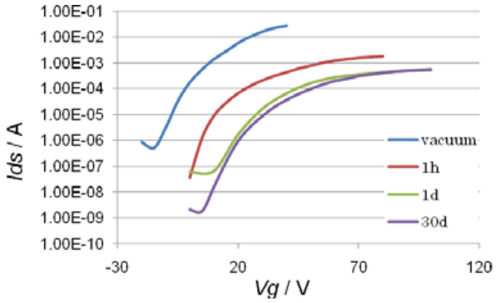


Figure S9. Transfer plots of **3** (T_{sub} = r.t).

Table S4. FET characteristics of **3** (BC) in air[a]

Compd.	Time in air	μ(cm^2/Vs)	I_{on}/I_{off}	V_{th} V
3	vacuum	0.405	5.3x10^4	5.6
	1h	7.6x10^{-3}	5.0x10^4	11
	1d	2.8x10^{-3}	8.6x10^3	21
	30d	2.3x10^{-3}	2.6x10^5	25

[a]Stored and measured in air.

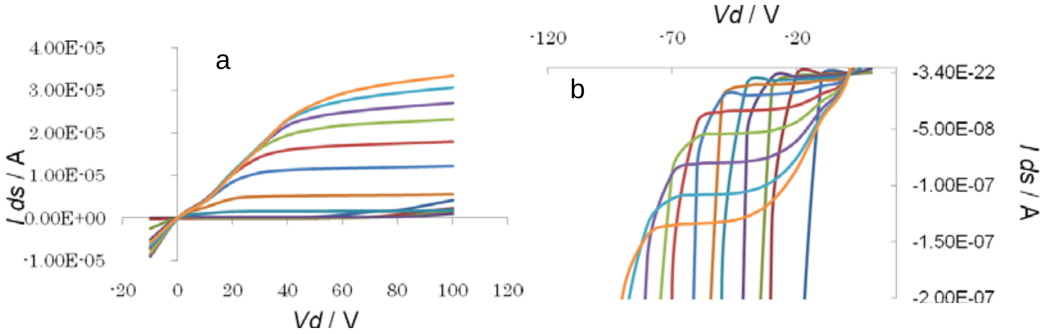


Figure S10. Output plots of **1**. Hole mobility was calculated with $V_d = 60$ V.

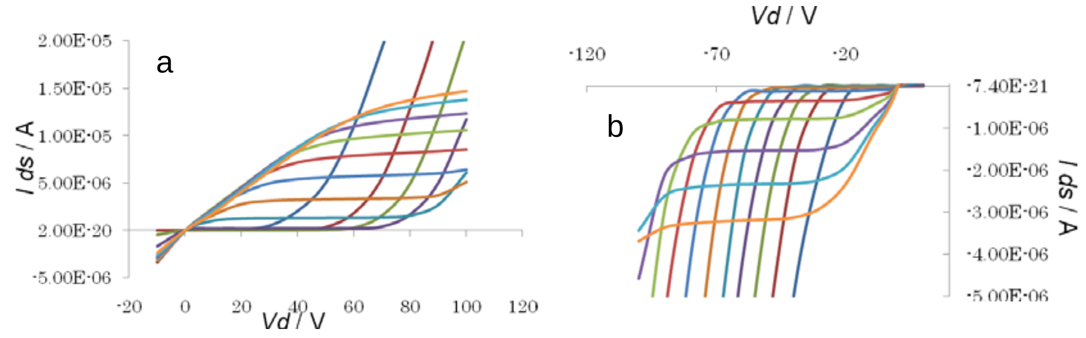


Figure S11. Output plots of **2**. Hole mobility was calculated with $V_d = 60$ V.

The X-ray measurement of **2** was carried out using a RAXIS-RAPID imaging plate diffractometer with Mo-Ka radiation (λ= 0.71075 Å) at 93 K. Absorption collection for the data was applied using an empirical procedure. The structure was solved by the direct method (SIR2004) and refined by the full-matrix least-squares method on F^2. All calculations were performed using the CrystalStructure crystallographic software package except for refinement, which was performed using SHELXL-97.

Structural disorders were observed for two terminal benzo[*b*]thiophene units of **2** by 180-degree rotation around C-C bond axis, and the structural analysis could be converged by assuming contribution of two minor benzo[*b*]thiophene confomers (17%: S3A-C7A-C8A-C9A-C10A-C11A-C12A-C13A-C14A and 12%: S4A-C15A-C16A-C17A-C18A-C19A-C20A-C21A-C22A). Non-hydrogen atoms of a benzobisthiadiazole center and major conformers of the benzo[*b*]thiophene units were refined anisotropically. The minor conformers of benzo[*b*]thiophene units were refined isotropically. Hydrogen atoms were refined using the riding model.

Two alerts A observed in CIF check were attributed to the quite substantial disorder of the benzo[*b*]thiophene moieties. The best procedure was to treat the minor conformers as isotropic.

1, Isotropic non-H Atoms in Main Residue(s) ....18.

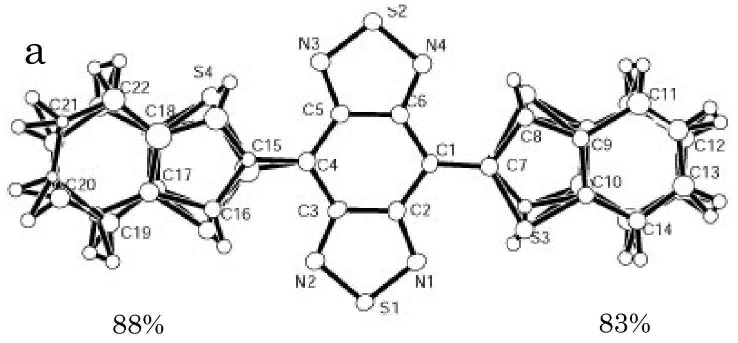
2, Large Non-Solvent C Ueq(max)/Ueq(min) ... 10.00 Ratio.

Crystal Data

Empirical Formula: $C_{22}H_{10}N_4S_4$
Formula Weight: 458.59
Crystal Color, Habit: blue, block
Crystal Dimensions: 0.30 X 0.10 X 0.05 mm
Lattice Parameters: a = 7.0940(3) Å
b = 13.9197(5) Å
c = 18.7501(9) Å
V = 1851.49(14) Å^3
Space Group: $P2_12_12_1$ (#19)
Z value: 4
D_{calc}: 1.645 g/cm^3
F_{000}: 936.00
No. Observations (All reflections): 4238

No. Variables: 288
Reflection/Parameter Ratio: 14.72
Residuals: R1 (I>2.00s(I)): 0.0362
Residuals: R (All reflections): 0.0511
Residuals: wR2 (All reflections): 0.0865
Goodness of Fit Indicator: 1.055

Major conformers (%)



Minor conformers (%)

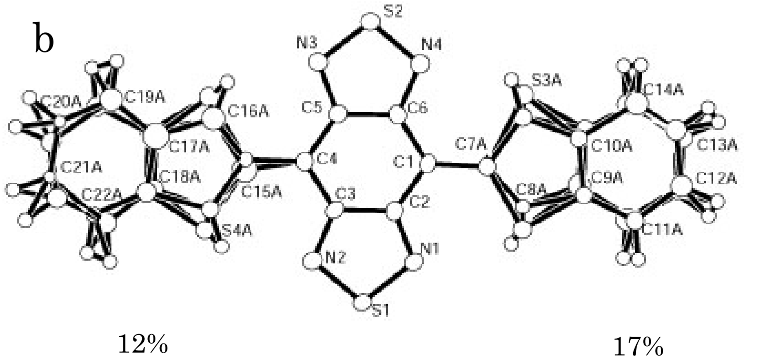


Figure S12. Disorder ratio of benzo[*b*]thiophene units of **2**, major conformers (a) and minor conformers (b).

References
S1: Preparation of 5, and stannyl reagents.
a) Y.Yamashita, K. Ono, M. Tomura, S. Tanaka, *Tetrahedrom.* 1997, **53**, 10169.
b) S.Ando, J. Nishida, H. Tada, Y. Inoue, S.Tokito, Y. Yamashita, *J.Am. Chem. Soc.* 2005, **127**, 5336.
c) Fargeas, V. Favresse, F. Mathieu, D. Beaudet, I. Charrue, P. Lebret,B. Piteau, M. Quintard, J-P. *Eur. J. Org. Chem.* 2003, 1711.
S2: Kitamura,C. Tanaka, S. Yamashita, Y. Chem. Mater. 1995, *8*, 570.