Supporting Information for

Methylthionated Benzo[1,2-*b*:4,5-*b'*]dithiophenes: Model Study to Control Packing Structures and Molecular Orientation in Thienoacene-Based Organic Semiconductors

Chengyuan Wang,*a Hiroshi Nakamura,a,b Hiroyoshi Sugino,a Kazuo Takimiya*a,c

^a Emergent Molecular Function Research Group, RIKEN Center for Emergent Matter Science (CEMS), 2-

- 1 Hirosawa, Wako, Saitama 351-0198 Japan
- ^b Nippon Kayaku Co., Ltd., 31-12 Shimo 3-Chome, Kita-ku, Tokyo 115-8588 Japan
- ^c Department of Chemistry, Graduate School of Science, Tohoku University, 6-3 Aoba, Aramaki, Aoba-
- Ku, Sendai, Miyagi 980-8578 Japan

E-mail: chengyuan.wang@riken.jp; takimiya@riken.jp

Experimental section

Materials

The chemical reagents and solvents were used as received from commercial sources without further purification except additional notification. Tetrahydrofuran (THF) was purified by a Glass Contour solvent purification system. Benzo[1,2-*b*,4,5-*b*']dithiophene (**BDT**) and 1,4-bis(methylthio)-2,5-bis[(trimethylsilyl)ethynyl]benzene (**1**) were prepared based on a literature reported method.^{S1}

Synthesis



Scheme S1. Synthetic route for α -MT-BDT

2,6-Bis(methylthio)benzo[1,2-*b*, 4,5-*b*']dithiophene (*α*-MT-BDT)

In a 3-neck flask, **BDT** (500 mg, 2.63 mmol) and THF (100 mL, anhydrous) were added, and the resulting solution was bubbled with nitrogen gas for 30 minutes. The solution was cooled down to 0 °C in iced-bath, and *n*-BuLi (1.6 M in hexane, 5.0 mL) was added dropwise over 5 minutes. The solution was maintained at room temperature for 1 hour, and dimethyl disulfide (0.8 mL, 9.0 mmol) was added dropwise. The solution was kept at room temperature for another 1 hour, after that H₂O (100 mL) was added, and the resulting solution was extracted with CH₂Cl₂ (50 mL × 3).The extracts were collected, dried by MgSO₄, and evaporated to give a crude product, which was purified by flash column chromatography (silica gel, hexane) to give pale yellow crystals (639mg, 86%). Mp. 236.2 °C; ¹H NMR $\delta_{\rm H}$ (CDCl₃, 400 MHz) 7.97 (2H, d, *J* = 0.5 Hz, Ar-H), 7.17 (2H, d, *J* = 0.5 Hz, Ar-H), 2.16 (6H, s, CH₃ × 2); ¹³C NMR $\delta_{\rm C}$ (CDCl₃, 100 MHz) 140.05, 138.09, 137.20, 123.19, 115.06, 19.81; HR-MS (EI⁺) *m/z* [M⁺] found 281.9670, formula C₁₆H₁₄S₄ [M⁺] calc. 281.9665.

3,7-Bis(methylthio)benzo[1,2-*b*, 4,5-*b*']dithiophene (*β***-MT-BDT**)

In a 3-neck flask which was degassed 3 times with argon, CH₂Cl₂ (20 mL, anhydrous) and S₂Cl₂ (2.4 mL, 30.04 mmol) were added successively. 1,4-bis(methylthio)-2,5-bis[(trimethylsilyl)ethynyl]benzene (1) (1.81 g, 4.99 mmol) was dissolved in CH₂Cl₂ (30 mL, anhydrous) and added to the solution dropwise over 35 minutes, and the resulting mixture was kept at room temperature for further 4 hours. CH₂Cl₂ was removed by bubbling nitrogen gas, and THF (150 mL, anhydrous) and MeOH (50 mL, anhydrous) were added, followed by addition of iodomethane (15 mL, 240.91 mmol), and the mixture was cooled down to 0 °C. NaBH₄ (5.68 g, 150.26 mmol) was added in small portions, and the resulting mixture was stirred overnight and allowed to warm to room temperature. The reaction was quenched by pouring solution into iced HCl (0.5 M, 200 mL), which was extracted with CH_2Cl_2 (50 mL \times 3). After the evaporation of solvents the residue was dissolved in THF (40 mL), and tetrabutylammonium fluoride (ca. 1M, 40 mL in THF) was added to the solution. The resulting solution was stirred at room temperature for 3 hours, and then poured into water and extracted with CH_2Cl_2 (50 mL \times 3). After evaporation, the crude product was purified by reprecipitation from MeOH and washed with diethyl ether to give a white solid (684 mg, yield 48%). Mp, 180.1 °C; ¹H NMR $\delta_{\rm H}$ (CDCl₃, 400 MHz) 8.35 (2H, s, Ar-H), 7.28 (2H, s, Ar-H), 2.57 (6H, s, CH₃ × 2); ¹³C NMR δ_C (CDCl₃, 100 MHz) 137.56, 136.80, 128.29, 123.80, 116.44, 17.59; HR-MS (EI⁺) *m/z* [M⁺] found 281.9671, formula C₁₂H₁₀S₄ [M⁺] calc. 281.9665.

Methods & Instruments

Nuclear magnetic resonance (NMR) spectra were recorded on a JEOL RESONACE JNM-ECS400 spectrometer operating at 400 MHz for ¹H or 100 MHz for ¹³C with TMS as internal reference. HR-MS was carried out in Materials Characterization Support Unit, RIKEN Advanced Technology Support Division. Melting points were uncorrected. UV-vis spectra were recorded on a Shimadzu UV-3600 spectrometer. Cyclic voltammograms (CVs) were recorded on a ALS Electrochemical Analyzer Model 612D in benzonitrile with tetrabutylammonium hexafluorophosphate (Bu₄NPF₆, 0.1 M) as supporting electrolyte at a scanning rate of 100 mV/s. Pt was used as working and counter electrodes, and Ag/AgCl was used as reference electrode. Ferrocene/ferrocenium redox couple (Fc⁺/Fc) was used as external

reference. Single-crystal X-ray analysis was carried on a Rigaku Rapid-IP (MoK α radiation, $\lambda = 0.71069$ Å, graphite monochromator, $2\theta_{max} = 55.0^{\circ}$). The structure was solved by direct methods. Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were included in the calculations but not refined. All calculations were performed using the crystallographic software package CrystalStructures4.2.^{S2} Theoretical calculations were carried out by DFT method at the B3LYP/6-31G(d) level using Gaussian 09 program package.^{S3} Thin film X-Ray Diffractions (XRD) patterns were obtained with a Rigaku Ultima-IV diffractometer with a Cu K α source ($\lambda = 1.541$ Å) in air. OFETs were fabricated on heavily doped n⁺-Si (100) wafer with a 200 nm thermally grown SiO₂ ($C_i = 17.3 \text{ nF cm}^{-2}$). The substrate surface was treated with octadecyltrichlorosilane (ODTS). Single crystals of α -MT-BDT, β -MT-BDT were directly grown on the substrates by physical vapor transport method. The thickness of the as-prepared single crystals is ~ 100 -300 nm for *a*-MT-BDT; and ~ 500 - 800 nm for *β*-MT-BDT, respectively. On the top of the crystals, gold (80 nm) as drain and source electrodes were deposited through a shadow mask by copper grid. The channel direction is along a axis for α -MT-BDT based single-crystal OFETs (Figure S15), but c axis for β -MT-BDT based single-crystal OFETs (Figure S16). Characteristics of the OFETs were measured at room temperature under ambient conditions with a Keithley 4200 semiconducting parameter analyzer. Fieldeffect mobility (μ) was calculated in the saturation regime using the following equation, $I_D = Ci\mu(W/2L)(V_G)$ $-V_{th}$)², where Ci is the capacitance of the SiO₂ insulator, and V_G and V_{th} are the gate and threshold voltages, respectively.

Figures







Figure S2. ¹³C NMR spectra of α -MT-BDT.



Figure S3. ¹H NMR spectra of β -MT-BDT.



Figure S4. ¹³C NMR spectra of β -MT-BDT.



Figure S5. Molecular structures and calculated HOMO and LUMO of parent BDT, *a*- and *β*-MT-BDT

(DFT B3LYP/6-31g(d) level).



Figure S6. UV-vis absorbance spectra of α -MT-BDT and β -MT-BDT in CHCl₃.



Figure S7. Cyclic voltammograms (CVs) of α -MT-BDT and β -MT-BDT in benzonitrile.

Fable S1. Summarized	energy	levels of	f α-MT-]	BDT a	and ß-	·MT-]	BDT

	HOMO (eV) ^a	LUMO (eV) ^b	Bandgap (eV) ^c	
BDT d	-5.60	-2.00	3.60	
α-MT-BDT	-5.30	-1.85	3.45	
β-MT-BDT	-5.45	-2.03	3.42	

^a Determined from CVs

^b Estimated by the equation $E_{\text{LUMO}} = E_{\text{HOMO}} + E_{\text{g}}$

^c Determined from λ_{onset} in UV-vis spectra

^d Data from reference S1



Figure S8. Molecular structures of α - (a/b: major/minor polymorph) and β -MT-BDT (c).



Figure S9. Definition of "edge" & "end" of α - (a/b: major/minor polymorph) and β -MT-BDT (c).



Figure S10. S-S contact in the crystal structure of β -MT-BDT.



Figure S11. XRD patterns of *α*-MT-BDT crystals on ODTS modified SiO₂/Si substrate.



Figure S12. XRD patterns of β -MT-BDT crystals on ODTS modified SiO₂/Si substrate.

Table S2. Summarized parameter	rs of MT-BDT s based SC-OFETs
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Compound	Mobility (cm ² V ⁻¹ s ⁻¹)	$V_{\rm th}({ m V})$	ON/OFF	
α-MT-BDT	$\mu_{ave} = 1.3 \times 10^{-2}$ $\mu_{max} = 2.3 \times 10^{-2}$	-10.0	~10 ⁵	
β-MT-BDT	$\mu_{\rm ave} = 2.2 \times 10^{-1}$	-21.5	~10 ⁵	
	$\mu_{\rm max} = 3.8 \times 10^{-1}$	-21.5		



Figure S13. Output curves of *α*-MT-BDT single-crystal based OFETs.



Figure S14. Output curves of β -MT-BDT single-crystal based OFETs.



Figure S15. The facets of a typical α -MT-BDT single crystal and its corresponding angle between

different planes from packing pattern.



Figure S16. The facets of a typical β -MT-BDT single crystal and its corresponding angle between different planes from packing pattern.

References

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S3. Gaussian 09, Revision D.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.