

Facile Synthesis of Highly π -Extended Heteroarenes, Dinaphtho[2,3-*b*:2',3'-*f*]chalcogenopheno[3,2-*b*]chalcogenophenes, and Their Application to Field-Effect Transistors

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1. Experimental details

Synthesis

General: All chemicals and solvents are of reagent grade unless otherwise indicated. THF was distilled from sodium benzophenone ketyl prior to use. Nuclear magnetic resonance spectra were obtained in deuterated chloroform with a JEOL Lambda 400 spectrometer operating at 400 MHz for ^1H with TMS as internal reference; chemical shifts (δ) are reported in parts per million. EI-MS spectra were obtained on a Shimadzu QP-5050A spectrometer using an electron impact ionization procedure (70 eV). The molecular ion peaks of the sulfur-containing or selenium compounds showed a typical isotopic pattern, and all the mass peaks are reported based on ^{32}S or ^{80}Se , respectively, unless otherwise stated. Solubility of DNTT and DNSS in dichloromethane was determined as follows: UV-vis spectra of saturated solution of DNTT and DNSS were measured. Concentration of the saturated solution calculated using the absorbance at 297 nm (DNTT) or 286 nm (DNSS) and molar absorption coefficient (ϵ) was converted into solubility (mg / L).

3-Methylthio-2-naphthaldehyde (1a)^{S1}

Caution! This procedure involves use of dimethyl disulfide, which is very stinking. Therefore, this must be carried out in a well-ventilated fume hood with disposable gloves. To a solution of *N,N,N'*-trimethylethylenediamine (2.87 ml, 21.0 mmol) in THF (35 mL) was added butyllithium (13.2 ml of 1.59M solution in hexane, 21.0 mmol) at $-30\text{ }^\circ\text{C}$. After the mixture was stirred for 15 min at the

same temperature, a solution of 2-naphthaldehyde (2.0 g, 12.8 mmol) in THF (10 mL) was slowly added over a period of 5 min, and then additional butyllithium (24.15 mL of 1.59M solution in hexane, 38.4 mmol) was added, and the resting mixture was stirred for 3.5 h at $-30\text{ }^{\circ}\text{C}$. Excess dimethyl disulfide (5.67 mL, 64 mmol) was then added, and after stirring at room temperature for 2h, 1M hydrochloric acid (20 mL) was added. The resulting mixture was stirred for 10 h and was extracted with dichloromethane (20 mL \times 3). The combined extracts were dried (MgSO_4) and concentrated in vacuo. The residue was purified by column chromatography on silica-gel eluted with hexane-ethyl acetate (9:1, v/v, $R_f = 0.3$) to give **1a** as yellow solid (1.49 g, 58% isolated yield). mp $53.5\text{--}54.5\text{ }^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 2.60 (s, 3H, SMe), 7.50 (ddd, 1H, $J = 8.2, 6.9, 1.3\text{ Hz}$, ArH), 7.618 (s, 1H, ArH), 7.623 (ddd, 1H, $J = 8.2, 6.9, 1.3\text{ Hz}$, ArH), 7.80 (brdd, 1H, $J = 8.2, 1.3\text{ Hz}$, ArH), 7.94 (brdd, 1H, $J = 8.2, 1.3\text{ Hz}$, ArH), 8.33 (s, 1H, ArH), 10.36 (s, 1H, CHO); ^{13}C NMR (100 MHz, CDCl_3) δ 15.1, 122.7, 125.7, 126.4, 128.9, 129.2, 129.4, 130.8, 135.5, 136.4, 136.9, 191.3; IR (KBr) $\nu = 1699\text{ (C=O)}, 1620, 1433, 1169, 1026, 872, 776, 756\text{ cm}^{-1}$; EIMS (70 eV) $m/z = 202\text{ (M}^+)$; Anal. Calcd for $\text{C}_{12}\text{H}_{10}\text{OS}$: C, 71.25; H, 4.98%. Found: C, 71.05; H, 4.83%.

3-Methylseleno-2-naphthaldehyde (1b)

Caution! This procedure involves use of toxic selenium as a key reagent and potentially produces organoselenium byproducts, which are highly toxic and stinking. It is advisable to avoid direct contact to the reagent and the byproducts with the skin. Thus, this procedure must be carried out in an efficient fume hood with disposable gloves and chemical-resistant safety goggles.

The title compound was synthesized by a similar procedure for **1a**. A mixed reagent of selenium powder and methyl iodide was employed instead of dimethyl disulfide; 32% isolated yield; yellow solid; mp $52.0\text{--}52.5\text{ }^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 2.37 (s, 3H, SeMe (d, $J_{\text{Se-H}}^{77} = 13.5\text{ Hz}$)), 7.50 (ddd, 1H, $J = 8.1, 6.8, 1.3\text{ Hz}$, ArH), 7.62 (ddd, 1H, $J = 8.1, 6.8, 1.3\text{ Hz}$, ArH), 7.69 (s, 1H, ArH), 7.77 (brdd, 1H, $J = 8.1, 1.3\text{ Hz}$, ArH), 7.91 (brdd, 1H, $J = 8.1, 1.3\text{ Hz}$, ArH), 8.26 (s, 1H, ArH), 10.22 (brs, 1H, CHO); ^{13}C NMR (100 MHz, CDCl_3) δ 5.9, 126.08, 126.12, 126.7, 129.1, 129.8, 130.0, 131.5, 132.6, 136.0, 138.3, 192.5; IR (KBr) ν 1684 (C=O), 1671, 1624, 1445, 1253, 1171, 1005, 882, 776, 741 cm^{-1} ; EIMS (70 eV) $m/z = 250\text{ (M}^+)$; Anal. Calcd for $\text{C}_{12}\text{H}_{10}\text{OSe}$: C, 57.84; H, 4.05%. Found: C, 57.85; H, 3.84%.

trans-1,2-Bis(3-methylthio-2-naphthyl)ethene (2a)^{S2}

To an ice-cooled suspension of zinc powder (0.39 g, 6.0 mmol) in THF (10 mL), titanium tetrachloride (0.66 mL, 6.0 mmol) was slowly added, and the resulting mixture was refluxed for 1.5 h. After cooling to room temperature, a solution of **1a** (0.405 g, 2.0 mmol) in THF (10 mL) was slowly added to the mixture, and the mixture was then refluxed for 10 h. After cooling to room temperature, the mixture was diluted with saturated aqueous sodium hydrogen carbonate solution (30 mL) and dichloromethane (30 mL) and stirred for 3.5 h. The mixture was filtered through a Celite pad, and the filtrate was separated into an organic and an aqueous layers. The aqueous layer was extracted with dichloromethane (20 mL \times 3), and the combined organic layer was dried (MgSO_4) and concentrated in vacuo. The resulting residue was

purified by passing through a silica-gel pad eluted with dichloromethane to give *trans*-1,2-bis(3-methylthio-2-naphthyl)ethene (**2a**) as yellow crystals (0.299 g, 80%). Analytical sample was obtained by recrystallization from dichloromethane. mp 195.0–196.0 °C; ¹H NMR (400 MHz, CDCl₃) δ 2.61 (s, 6H, SMe), 7.43 (ddd, 2H, *J* = 7.5, 7.5, 1.9 Hz, ArH), 7.46 (ddd, 2H, *J* = 7.5, 7.5, 1.9 Hz, ArH), 7.65 (s, 2H, ArH), 7.67 (s, 2H, CH=CH), 7.76 (dd, 2H, *J* = 7.5, 1.9 Hz, ArH), 7.86 (dd, 2H, *J* = 7.5, 1.9 Hz, ArH), 8.10 (s, 2H, ArH); ¹³C NMR (100 MHz, CDCl₃) δ 16.3, 124.1, 125.2, 125.6, 126.45, 126.54, 127.9, 128.5, 131.5, 133.4, 134.9, 135.9; IR (KBr) ν 1485, 1426, 1024, 957, 862, 741 cm⁻¹; EIMS (70 eV) *m/z* = 372 (M⁺), 357 (M⁺–Me), 325 (M⁺–SMe); Anal. Calcd for C₂₄H₂₀S₂: C, 77.37, H, 5.41%. Found: C, 77.07; H, 5.26%.

***trans*-1,2-Bis(3-methylseleno-2-naphthyl)ethene (2b)**

The title compound was synthesized from **1b** by a similar procedure for **2a**; 77% isolated yield. Pale yellow crystals; mp 199.0–199.5 °C; ¹H NMR (400 MHz, CDCl₃) δ 2.44 (s, 6H, SeMe (d, *J*_{Se-¹H} = 11.5 Hz)), 7.44–7.49 (m 4H, ArH), 7.63 (s, 2H, ArH), 7.75–7.76 (m, 2H, ArH), 7.86–7.88 (m, 4H, ArH and CH=CH), 8.10 (s, 2H, ArH); ¹³C NMR (100 MHz, CDCl₃) δ 7.8, 125.1, 125.9, 126.4, 126.6, 127.9, 128.9, 130.4, 130.7, 132.2, 133.4, 136.5; IR (KBr) ν 1487, 1424, 951, 862, 747, 735 cm⁻¹; EIMS (70 eV) *m/z* = 468 (M⁺); Anal. Calcd for C₂₄H₂₀Se₂: C, 61.81; H, 4.32%. Found: C, 61.82; H, 4.29%.

Dinaphtho[2,3-*b*:2',3'-*f*]thieno[3,2-*b*]thiophene (DNTT)

A solution of *trans*-1,2-bis(3-methylthio-2-naphthyl)ethene (**2a**, 0.2235 g, 0.60 mmol) and iodine (4.87 g, 19.2 mmol) in chloroform (15 mL) was refluxed for 21 h. After cooling to room temperature, saturated aqueous sodium hydrogen sulfite solution (20 mL) was added, and the resulting precipitate was collected by filtration and was washed with water and chloroform. The crude product was purified by vacuum sublimation (source temperature: 220 °C under ~10⁻³ Pa) to give analytical sample of DNTT as a yellow solid (0.173 g, 85%). Yellow crystals; mp >300 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.54–7.57 (m, 4H, ArH), 7.96–7.98 (m, 2H, ArH), 8.05–8.07 (m, 2H, ArH), 8.40 (s, 2H, ArH), 8.45 (s, 2H, ArH); IR (KBr) ν 1273, 872, 750, 739 cm⁻¹; EIMS (70 eV) *m/z* = 340 (M⁺), 170 (M⁺/2); Anal. Calcd for C₂₂H₁₂S₂: C, 77.61; H, 3.55%. Found: C, 77.40; H, 3.38%. Solubility in dichloromethane at rt: 3.44 mg / L.

Dinaphtho[2,3-*b*:2',3'-*f*]selenopheno[3,2-*b*]selenophene (DNSS)

The title compound was synthesized by a similar procedure for DNTT. 79% isolated yield after purification by vacuum sublimation (source temperature, 250 °C under ~10⁻³ Pa). Yellow crystals; mp >300 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.53–7.57 (m, ArH), 7.91–7.94 (m, ArH), 8.01–8.03 (m, ArH), 8.29 (s, ArH), 8.45 (s, ArH); IR (KBr) ν 1418, 1271, 1256, 874, 752 cm⁻¹; EIMS (70 eV) *m/z* = 436 (M⁺), 218 (M⁺/2); Anal. Calcd for C₂₂H₁₂Se₂: C, 60.85; H, 2.79. Found: C, 60.56; H, 2.60. Solubility in dichloromethane at rt: 2.80 mg / L.

Chemical Stability of DNTT and DNSS in solution

Saturated solutions of DNTT and DNSS in air-saturated dichloromethane were prepared, and their UV-vis spectra were recorded. Their UV-vis spectra were virtually no changed even after 48 h under ambient atmosphere in dark as shown in Figure S1. Pentacene, on the other hand, was rapidly degraded under the same experimental conditions with in 24 h as already reported (Figure S2).^{S3}

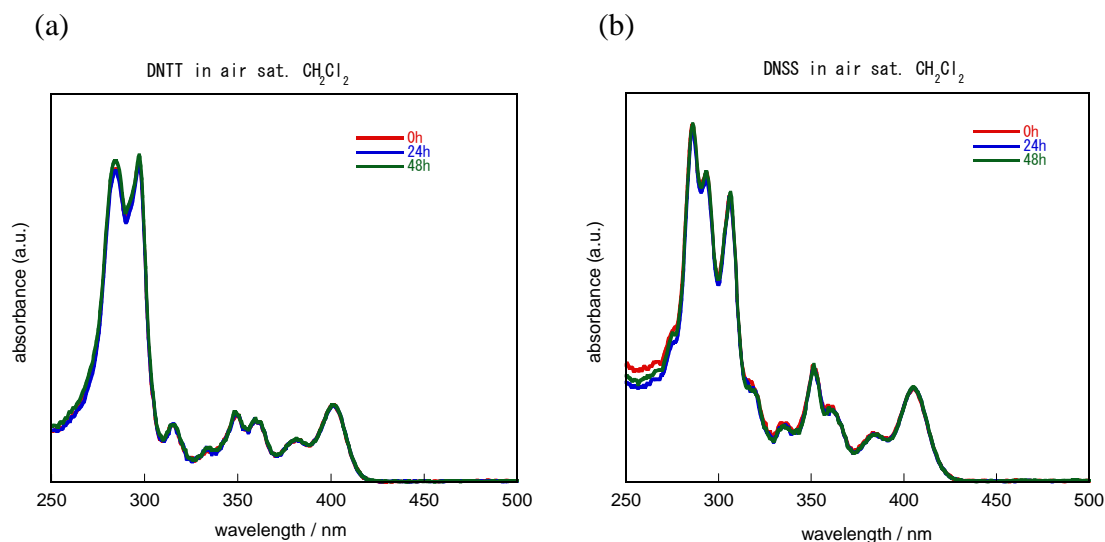


Figure S1. UV-Vis spectra of DNTT (a) and DNSS (b) in air-saturated dichloromethane solution.

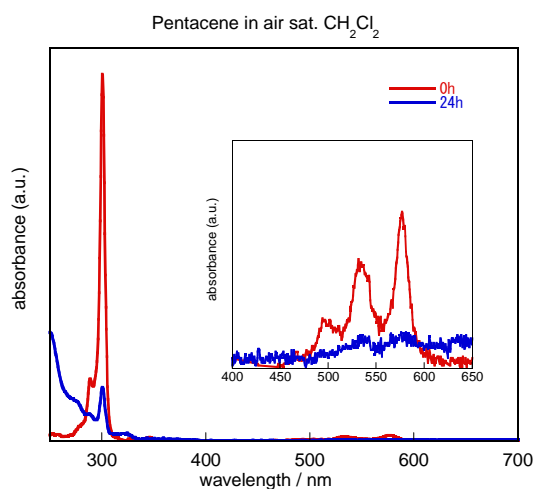


Figure S2. UV-Vis spectra of pentacene in air-saturated dichloromethane solution.

Characterization of DNTT and DNSS

Cyclic voltammograms (CVs) were recorded on a Hokuto Denko HA-301 potentiostat and a Hokuto Denko HB-104 function generator in benzonitrile containing tetrabutylammonium hexafluorophosphate (Bu_4NPF_6 , 0.1 M) as supporting electrolyte at a scan rate of 100 mV/s. Counter and working electrodes were made of Pt, and the reference electrode was Ag/AgCl. All the potentials were calibrated with the standard ferrocene/ferrocenium redox couple ($E^{1/2} = +0.46$ V measured under identical conditions). UV-vis spectra in CH_2Cl_2 solution or thin films were recorded on a Shimadzu UV-3100 spectrometer. Differential scanning calorimetry was carried out on a Seiko Instruments EXSTAR6000 DSC6200.

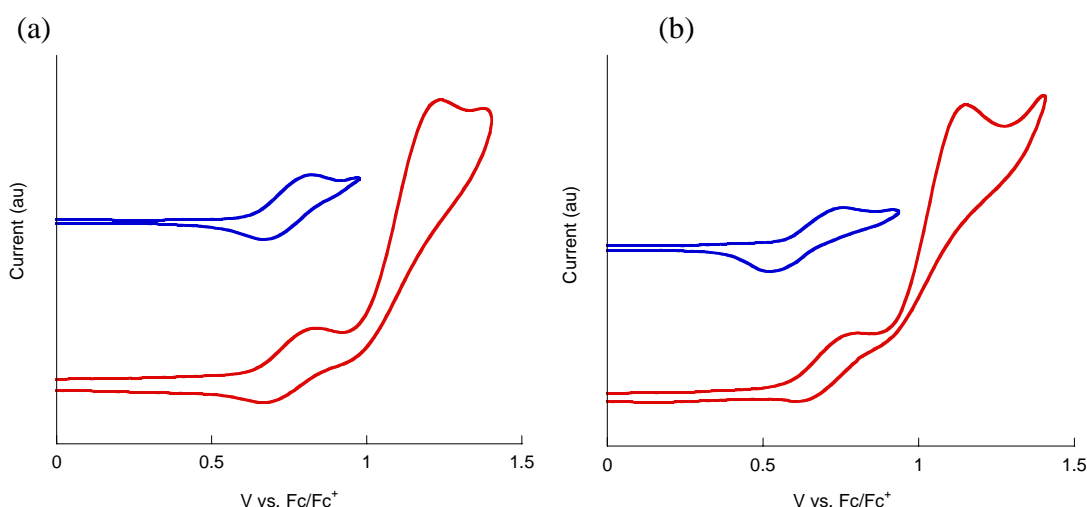


Figure S3. Cyclic voltammogram of DNTT (a) and DNSS (b). Scan ranges are 0~+1.0 V (blue traces) and 0~+1.5 V (red traces), respectively. The oxidation onsets are determined to be +0.62 V for DNTT and 0.58 V for DNSS, respectively.

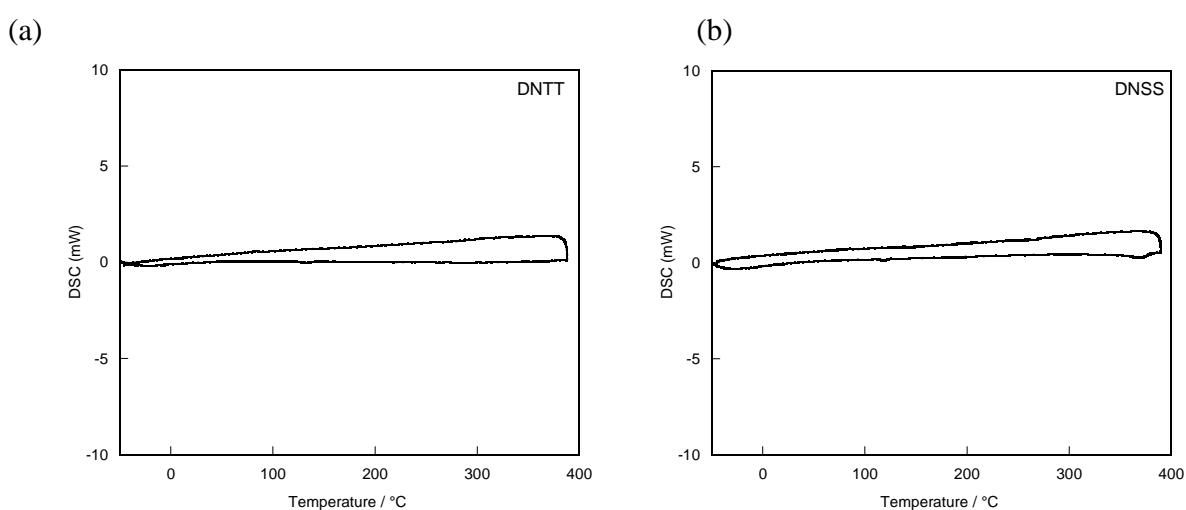


Figure S4. DSC trace of DNTT and DNSS. No thermal transition was observed up to 390 °C.

2. X-ray crystallographic analysis of DNTT

Single crystals were obtained by recrystallization from *m*-dichlorobenzene. The X-ray crystal structure analysis was made on a Rigaku Rapid-S imaging plate (MoK α radiation, $\lambda = 0.71069$ Å, graphite monochromator, $T = 296$ K, $2\theta_{\max} = 55.0^\circ$). The structure was solved by the direct methods.^{S4} 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 CrystalStructure 3.6.0.^{S5}

Crystal data for DNTT: C₂₂H₁₂S₂, $M = 340.46$, yellow plate, $0.35 \times 0.15 \times 0.03$ mm³, *Monoclinic*, space group $P2_1$ (no. 4), $a = 6.187(4)$, $b = 7.662(6)$, $c = 16.21(1)$ Å, $V = 767.7(9)$ Å³, $Z = 2$, $D_{\text{calc}} = 1.473$ gcm⁻³, $R = 0.044$ for 3374 observed reflections ($I > 2\sigma(I)$) and 230 variable parameters, $R_w = 0.068$ for all data.

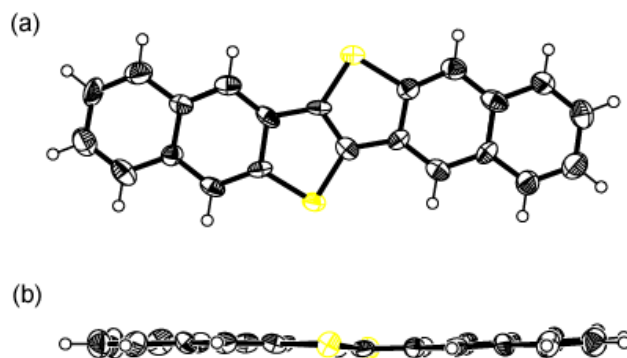


Figure S5. Molecular structure of DNTT: (a) top view; (b) side view.

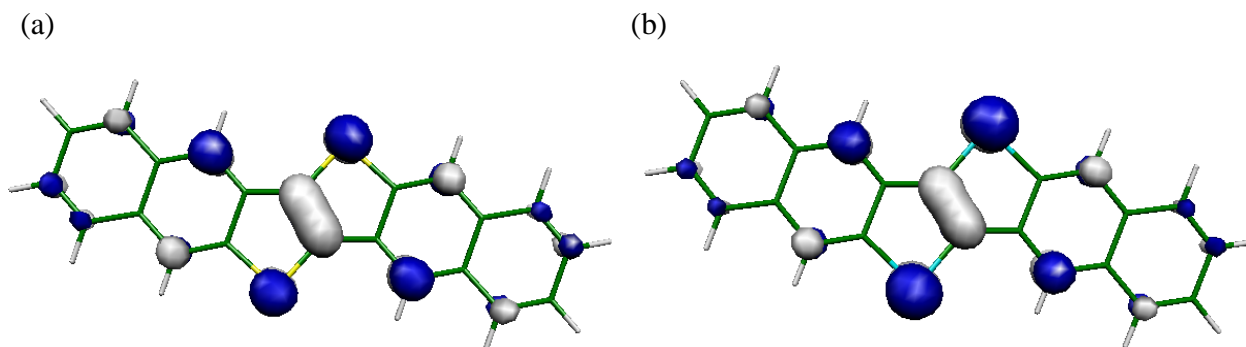
3. DFT calculations

MO calculations were carried out by DFT methods at the B3LYP-6-31G(d) level using the PC GAMESS program.^{S6}

The calculated HOMO and LUMO levels of DNTT and DNSS are listed in Table S1. These two compounds have similar energy levels of frontier orbitals as well as HOMO-LUMO gaps, indicating their similar electronic structures. These calculated values are qualitatively consistent with the data estimated experimentally using cyclic voltammetry and UV-Vis spectra.

Table S1. Calculated frontier levels of DNTT and DNSS.

	HOMO / eV	LUMO / eV	ΔE / eV
DNTT	−5.19	−1.81	3.38
DNSS	−5.13	−1.80	3.33

**Figure S6.** HOMO of DNTT (a) and DNSS (b).

4. Device fabrications and evaluations

The Si/SiO₂ substrates were treated in following ways; the substrate with an OTS (octyltrichlorosilane)-SAM (self-assembled monolayer) was obtained by immersing the Si/SiO₂ substrate in 0.1 M OTS in toluene at 60 °C for 20 min.^{S7} HMDS (hexamethyldisilazane)-treatments were carried out by exposing the silicon wafers to HMDS vapor at room temperature in a closed desiccator under nitrogen for 12h.^{S8} OFETs were fabricated in a “top-contact” configuration on a heavily doped *n*⁺-Si (100) wafer with 200-nm-thick thermally grown SiO₂ (*C_i* = 17.3 nF cm^{−2}). A thin film (50 nm thick) of DNTT or DNSS as the active layer was vacuum-deposited on the Si/SiO₂ substrates maintained at various temperatures (*T_{sub}*) at a rate of 1–2 Å s^{−1} under a pressure of ~2 × 10^{−3} Pa. On top of the organic thin film, gold films (80 nm) as drain and source electrodes were deposited through a shadow mask. For a typical device, the drain-source channel length (*L*) and width (*W*) are 50 μm and ca. 1.5 mm, respectively. The characteristics of the OFET devices were measured at room temperature in air with a Keithly 6430 subfemtoammeter and a Keithly 2400 source meter, operated by a LabTracer program and GPIB interface. Field-effect mobility (μ_{FET}) was calculated in the saturation regime (*V_d* = −60 V) of the *I_d* using the following equation,

$$I_d = (WC_i/2L) \mu_{\text{FET}} (V_g - V_{th})^2$$

where C_i is the capacitance of the SiO_2 insulator, and V_g and V_{th} are the gate and threshold voltages, respectively. Current on/off ratio (I_{on}/I_{off}) was determined from the I_d at $V_g = 0$ V (I_{off}) and $V_g = -60$ V (I_{on}). The μ_{FET} data reported in Table 1 are values from more than 10 different devices.

Table S2. FET characteristics of DNTT and DNSS devices fabricated on bare Si/SiO₂ substrate.

Compound	$T_{sub} / ^\circ\text{C}$	$\mu_{FET}^a / \text{cm}^2 \text{V}^{-1} \text{s}^{-1}$	I_{on}/I_{off}	V_{th} / V
DNTT	rt	0.13–0.24	5×10^6	-19 ± 9
	60	0.14–0.24	10^6	-9.0 ± 3.0
	100	0.22–0.24	5×10^5	-2.5 ± 1.5
DNSS	rt	0.13–0.14	10^5	-1.5 ± 2.5
	60	0.12–0.22	10^5	0 ± 1.0
	100	0.032–0.15	10^5	-4.5 ± 5.5

^a data from more than 10 devices.

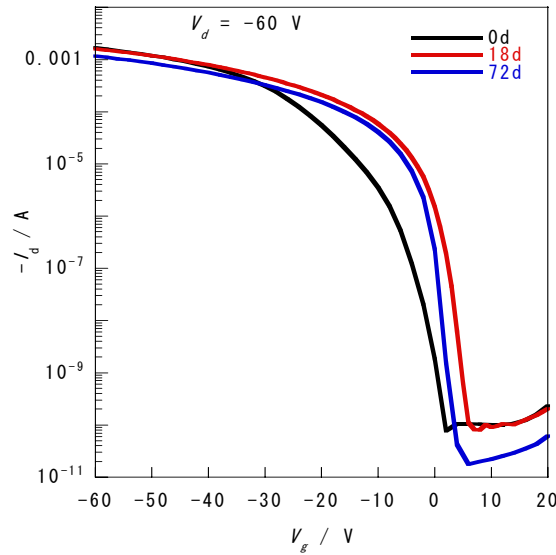
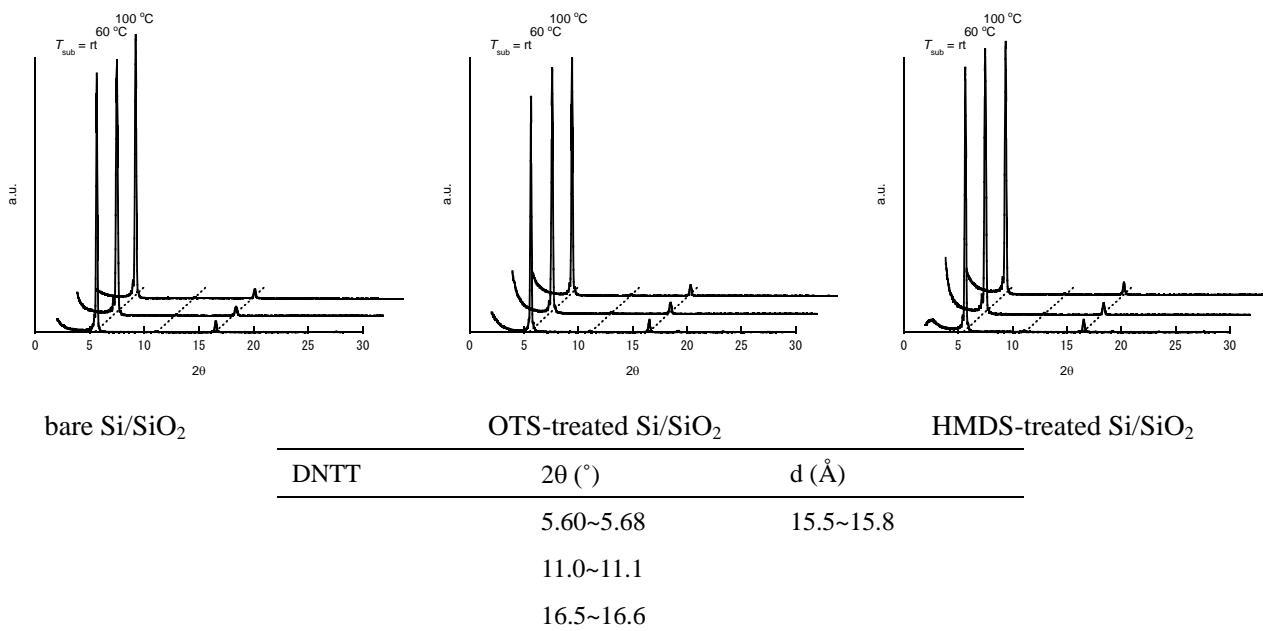


Figure S7. Transfer characteristics ($V_d = -60$ V) of DNTT-based OFETs on the OTS-treated substrate ($T_{sub} = 60$ °C) after storage 18 and 72 days under ambient conditions. It should be noted that the transfer characteristics after 72 days are virtually no changed, though the I_d is slightly reduced.

5. XRD and AFM images of evaporated thin films

X-ray diffractions of evaporated thin films deposited on the Si/SiO₂ substrates were obtained with a Rigaku RINT-2200 diffractometer with a Cu K α source ($\lambda = 1.541 \text{ \AA}$) in air. AFM images of thin films on Si/SiO₂ substrates were obtained by using a Molecular Imaging PicoPlus microscope in air.

a) DNTT



b) DNSS

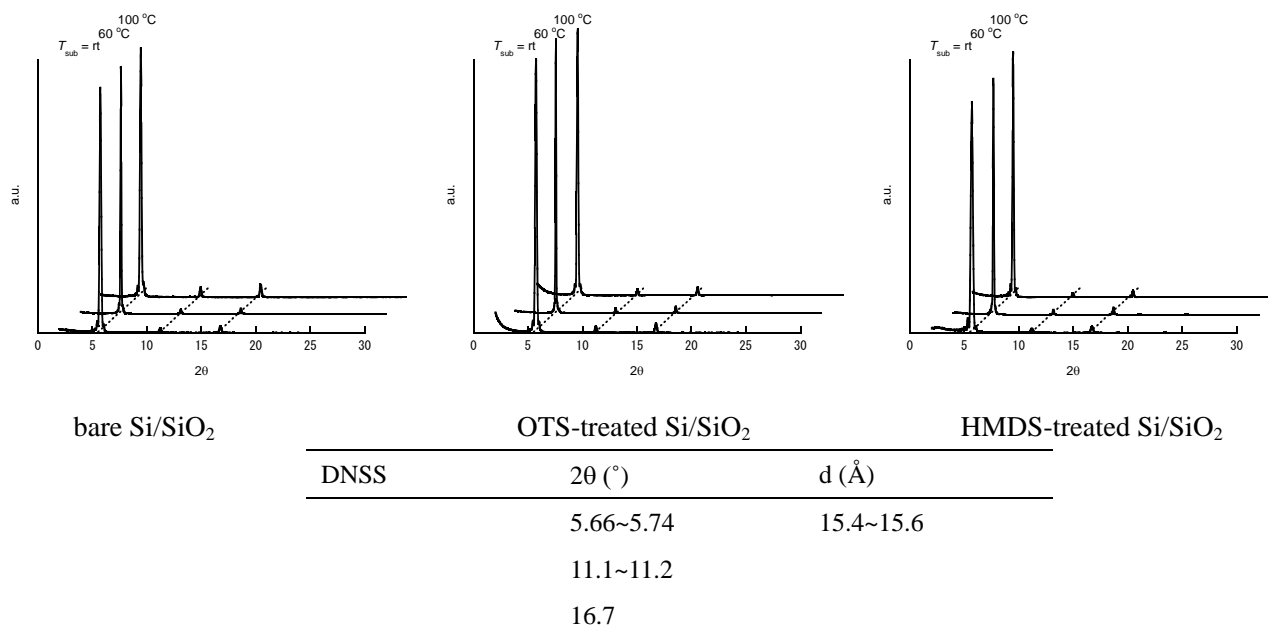
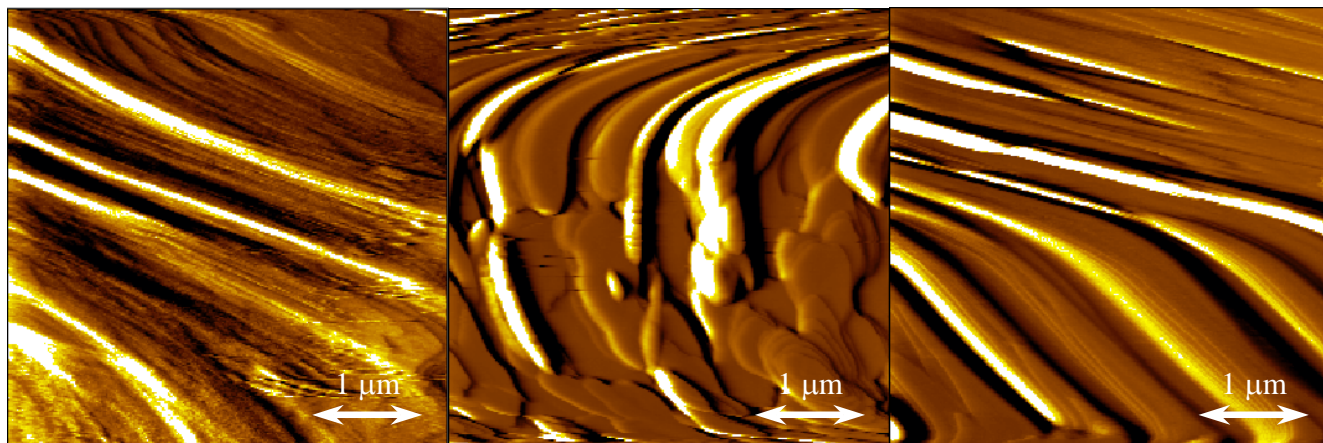


Figure S8. XRDs of evaporated thin film of DNTT and DNSS.

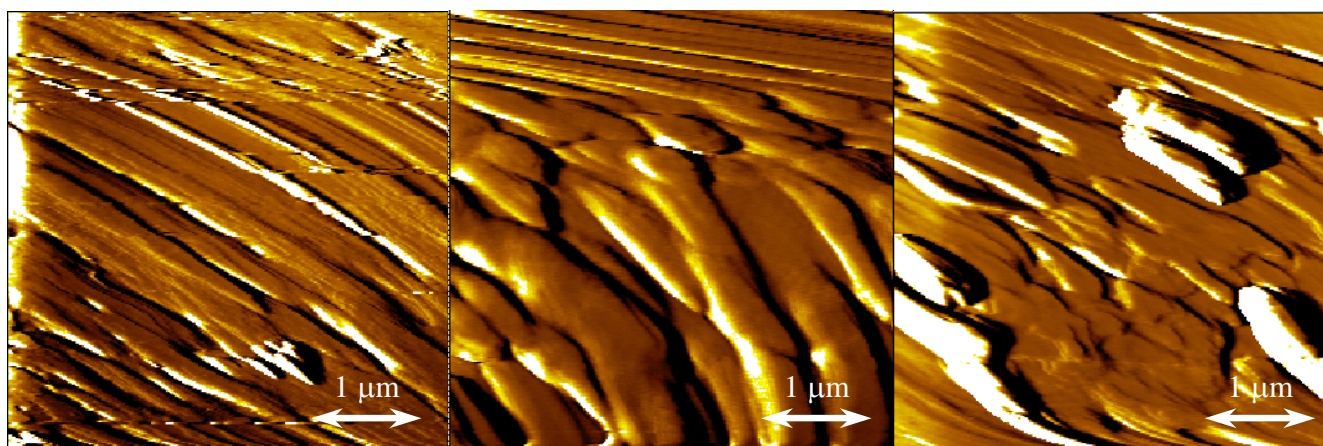
(a) DNTT



bare Si/SiO₂ ($T_{\text{sub}} = \text{rt}$)

OTS-treated Si/SiO₂ ($T_{\text{sub}} = \text{rt}$)

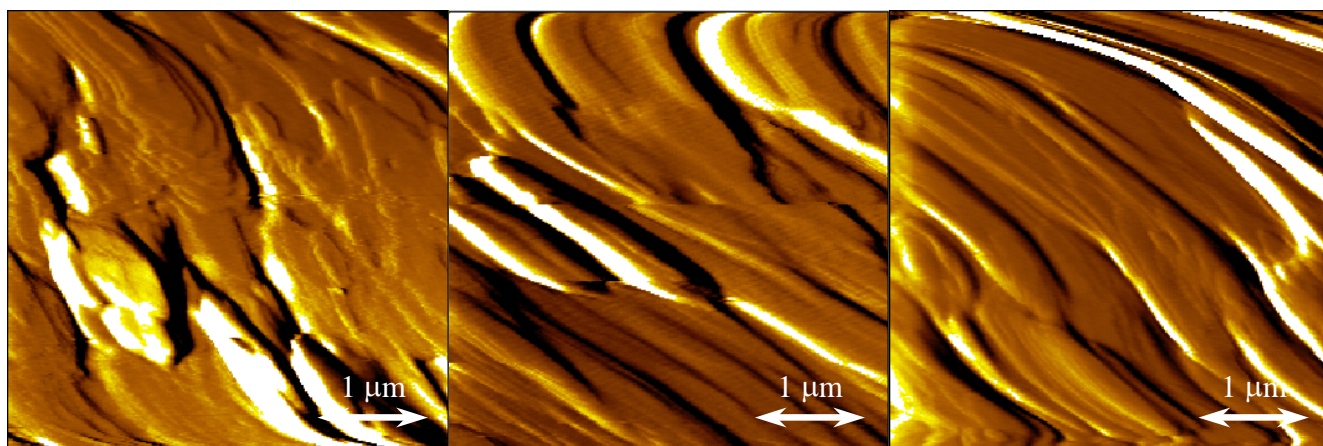
HMDS-treated Si/SiO₂ ($T_{\text{sub}} = \text{rt}$)



bare Si/SiO₂ ($T_{\text{sub}} = 60\text{ }^{\circ}\text{C}$)

OTS-treated Si/SiO₂ ($T_{\text{sub}} = 60\text{ }^{\circ}\text{C}$)

HMDS-treated Si/SiO₂ ($T_{\text{sub}} = 60\text{ }^{\circ}\text{C}$)

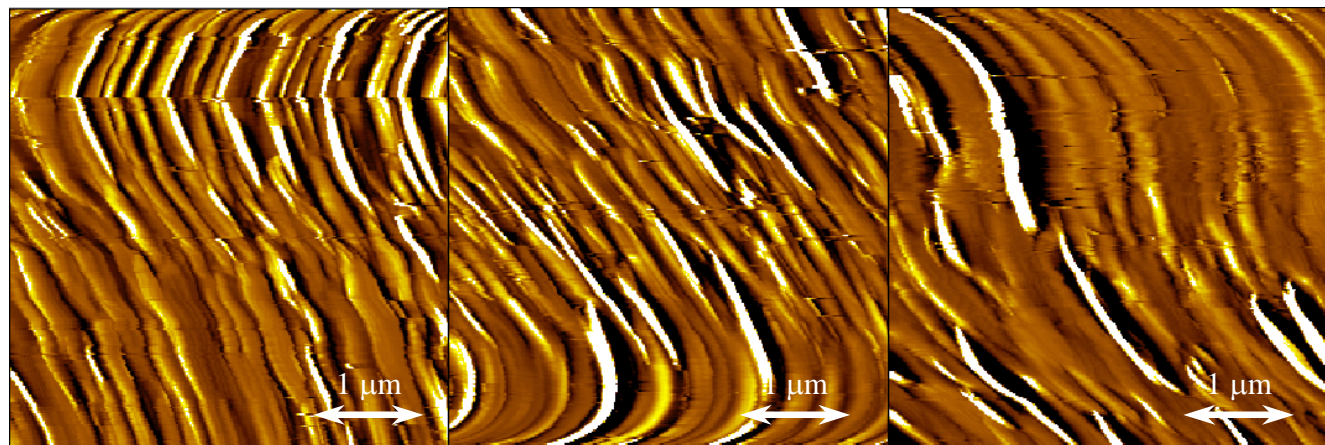


bare Si/SiO₂ ($T_{\text{sub}} = 100\text{ }^{\circ}\text{C}$)

OTS-treated Si/SiO₂ ($T_{\text{sub}} = 100\text{ }^{\circ}\text{C}$)

HMDS-treated Si/SiO₂ ($T_{\text{sub}} = 100\text{ }^{\circ}\text{C}$)

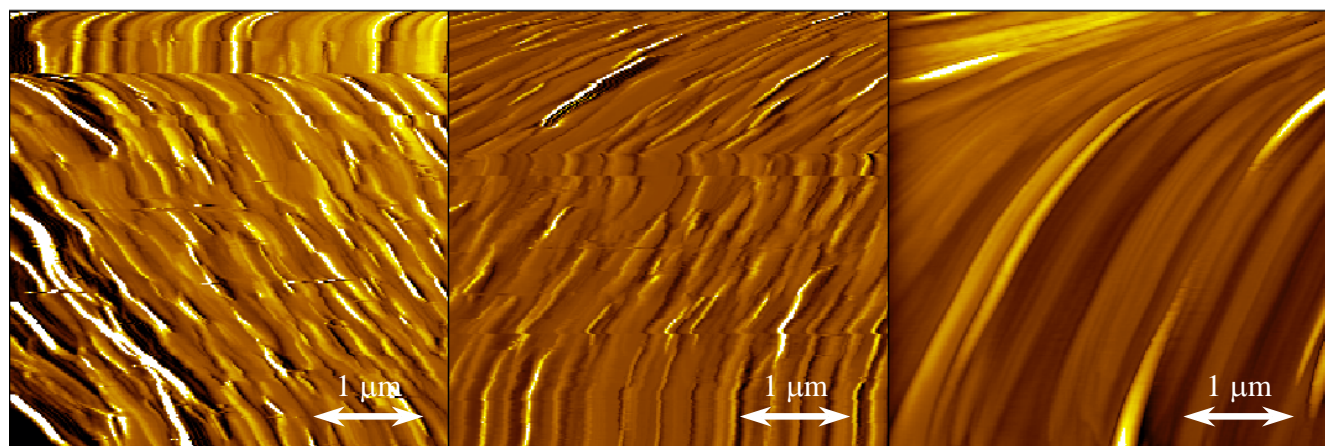
(b) DNSS



bare Si/SiO₂ ($T_{\text{sub}} = \text{rt}$)

OTS-treated Si/SiO₂ ($T_{\text{sub}} = \text{rt}$)

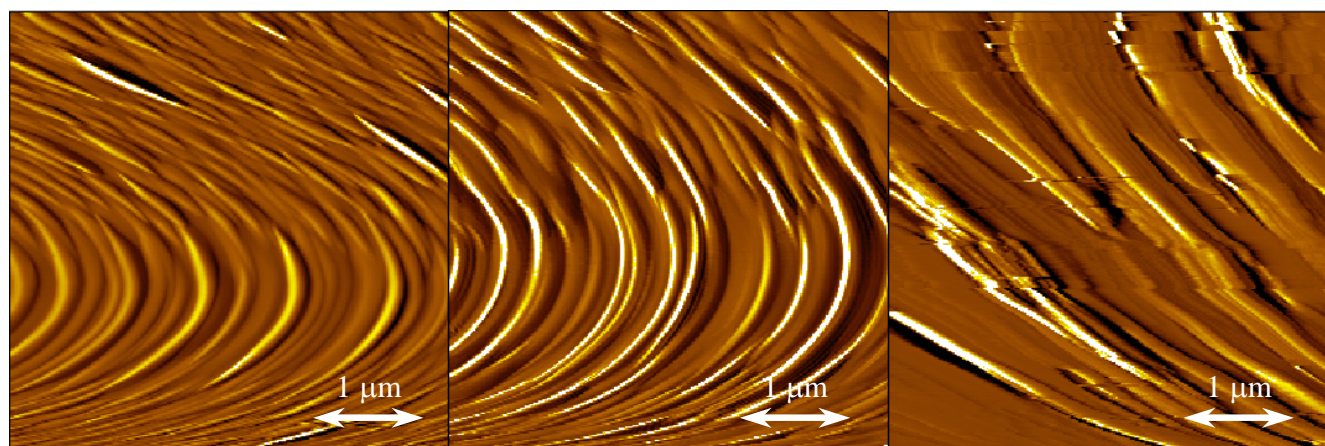
HMDS-treated Si/SiO₂ ($T_{\text{sub}} = \text{rt}$)



bare Si/SiO₂ ($T_{\text{sub}} = 60\text{ }^{\circ}\text{C}$)

OTS-treated Si/SiO₂ ($T_{\text{sub}} = 60\text{ }^{\circ}\text{C}$)

HMDS-treated Si/SiO₂ ($T_{\text{sub}} = 60\text{ }^{\circ}\text{C}$)



bare Si/SiO₂ ($T_{\text{sub}} = 100\text{ }^{\circ}\text{C}$)

OTS-treated Si/SiO₂ ($T_{\text{sub}} = 100\text{ }^{\circ}\text{C}$)

HMDS-treated Si/SiO₂ ($T_{\text{sub}} = 100\text{ }^{\circ}\text{C}$)

Figure S9. AFM images of evaporated thin film of DNSS.

7. References

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