Supporting Information for

Unique Three-Dimensional (3D) Molecular Array in Dimethyl-DNTT Crystals: a New Approach to 3D Organic Semiconductors

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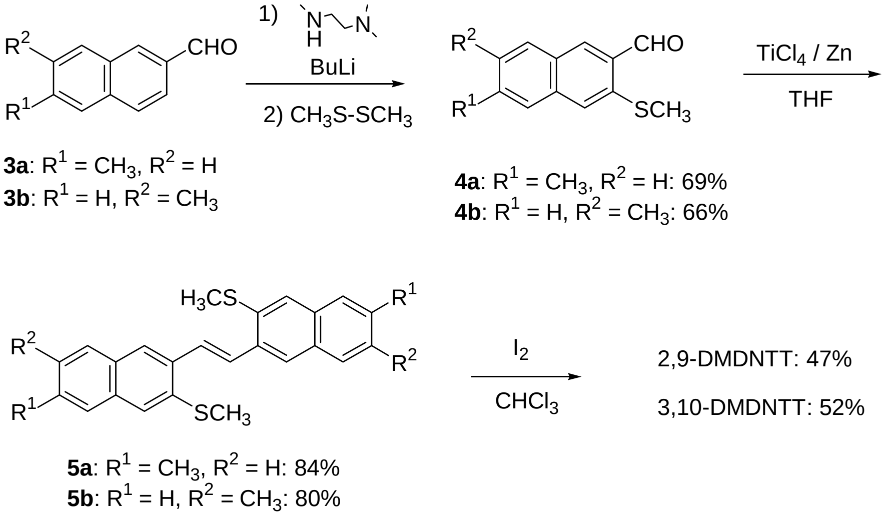
1. Synthesis of DMDNTTs



Scheme S1. Synthesis of DMDNTTs.

Experimental

General: All chemicals and solvents are of reagent grade unless otherwise indicated. DMF was distilled from CaH_2 under reduced pressure. 6-methyl- (**3a**) and 7-methyl- 2-naphthaldehyde (**3b**) were prepared according to the reported procedure.[S1] Melting points were uncorrected. Nuclear magnetic resonance spectra were obtained in deuterated chloroform with a JEOL EX-270 spectrometer operating at 270 MHz for ^{1}H 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 compounds showed a typical isotopic pattern, and all the mass peaks are reported based on ^{32}S.

6-Methyl-3-methylthio-2-naphthaldehyde (4a)

Caution! This procedure involves use of dimethyl disulfide, which emits a powerful stench. Therefore, this must be carried out in a well-ventilated fume hood with disposable gloves. To a solution of *N*,*N*,*N'*-trimethylethylenediammine (0.83 ml, 6.6 mmol) in THF (25 mL) was added butyllithium (4.0 ml of 1.66 M solution in hexane, 6.6 mmol) at –30 ºC. After the mixture was stirred for 15 min at the same temperature, a solution of 6-methyl-2-naphthaldehyde[S1] (4 mmol) in THF (12 mL) was slowly added over a period of 5 min, and then additional butyllithium (7.2 mL of 1.66 M solution in hexane, 12.0 mmol) was added, and the resting mixture was stirred for 3.5 h at –30 ºC. Excess dimethyl disulfide (1.8 ml, 20 mmol) was then added, and after stirring at room temperature for 23 h, 2M hydrochloric acid (20 mL) was added. The resulting mixture was stirred for 10 h and was extracted with dichloromethane (20 mL × 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 6-methyl-3-methylthio-2-naphthaldehyde.

62% isolated yield; pale yellow crystals from dichloromethane; mp 117–118 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.54 (s, 3H), 2.58 (s, 3H), 7.33 (dd, *J* = 8.4, 1.4 Hz, 1H), 7.53 (s, 1H), 7.58 (s, 1H), 7.83 (d, *J* = 8.4 Hz, 1H), 8.28 (s, 1H), 10.33 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.9, 22.3, 123.2, 126.2, 128.5, 128.9, 129.6, 131.2, 136.8, 137.0, 137.8, 140.8, 192.3; IR (KBr) ν = 1678 cm^{-1} (CHO);. EI-MS, *m/z* = 216 (M^+); Anal. Calcd for $C_{13}H_{12}OS$: C, 72.19; H, 5.59%. Found: C, 71.80; H, 5.43%.

7-Methyl-3-methylthio-2-naphthaldehyde (4b)

The title compound was obtained in the same manner as that for 6-methyl-3-methylthio-2-naphthaldehyde from 7-methyl-2-naphthaldehyde[S1].

66% isolated yield; pale yellow crystals from dichloromethane; mp 68–69 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.52 (s, 3H), 2.58 (s, 3H), 7.46 (d, *J* = 6.8, 1H), 7.59 (s, 1H), 7.69 (s, 1H), 7.71 (d, *J* = 6.8 Hz, 1H), 8.25 (s, 1H), 10.36 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.1, 21.9, 123.9, 126.9, 128.5, 130.5, 131.9, 132.6, 134.8, 136.3, 136.4, 136.5, 192.4; IR (KBr) ν = 1688 cm^{-1} (CHO);. EI-MS, *m/z* = 216 (M^+); Anal. Calcd for $C_{13}H_{12}OS$: C, 72.19; H, 5.59%. Found: C, 72.29; H, 5.57%.

***trans*-1,2-Bis(6-methyl-3-methylthionaphth-2-yl)ethylene (5a)**

To an ice-cooled suspension of zinc powder (0.35 g, 5.3 mmol) in THF (31 mL), titanium tetrachloride (0.6 mL, 5.3 mmol) was slowly added, and the resulting mixture was refluxed for 3 h. After cooling to room temperature, a solution of 6-methyl-3-methylthio-2-naphthaldehyde (0.58 g, 1.8 mmol) in THF (10 mL) was slowly added to the mixture, and the mixture was then refluxed for 24 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 chloroform (20 mL × 3), and the combined organic layer was dried ($MgSO_4$) and concentrated in vacuo. The resulting reside was purified by passing through a silica-gel pad eluted with dichloromethane to give *trans*-1,2-bis (3-methylthio-6-methylnaphth-2-yl)ethene as yellow crystals.

84% isolated yield; yellow crystals from dichloromethane-hexane; mp 185–186 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.51 (s, 6H), 2.59 (s, 6H), 7.29 (dd, J = 8.5, 1.9 Hz, 2H), 7.53 (s, 2H), 7.57 (s, 2H), 7.64 (s, 2H), 7.75 (d, J = 8.5 Hz, 2H), 8.05 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.6, 22.1, 124.1, 125.3, 126.0, 128.1, 128.2, 128.4, 128.6, 130.2, 134.0,136.2, 136.7; IR (KBr) ν = 1489, 1433, 947, 878 cm^{-1}; EI-MS, m/z = 400 (M^+); Anal. Calcd for $C_{26}H_{24}S_2$: C, 77.95; H, 6.04%. Found: C, 77.65; H, 5.84%.

trans-1,2-Bis(7-methyl-3-methylthionaphth-2-yl)ethylene (5b)

The title compound was obtained in the same manner as that for 6-methyl isomer from 7-methyl--3-methylthio-2-naphthaldehyde.

80% isolated yield; yellow crystals from dichloromethane-hexane; mp 218–219 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.51 (s, 6H), 2.58 (s, 6H), 7.29 (d, J = 7.6 Hz, 2H), 7.63 (s, 4H), 7.65 (d, J=7.6 Hz, 2H), 7.67 (s, 2H) 8.03 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ; IR (KBr) ν = 1490, 1437, 966, 874 cm^{-1};. EI-MS, m/z = 400 (M^+); Anal. Calcd for $C_{26}H_{24}S_2$: C, 77.95; H, 6.04%. Found: C, 77.56; H, 6.28%.

2,9-Dimethyldinaphtho[2,3-*b*:2',3'-*f*]thieno[3,2-*b*]thiophen (2,9-DMDNTT)

A solution of *trans*-1,2-bis(3-methylthio-6-methyl-2-naphthyl)ethene (0.15 mmol) and iodine (1.2 g, 4.6 mmol) in chloroform (10 mL) was stirred for 3 days. The mixture was concentrated in vacuo, and the residue was diluted with MeOH (20 mL) and stirred for 30 min at rt. The mixture was added to saturated aqueous sodium hydrogen sulfite solution (20 mL), and was stirred for 1h. The resulting precipitate was collected by filtration and was washed with water and chloroform. Extraction from the crude product using Soxhlet extractor gave yellow crystals of C_n-DNTT, which was further purified by vacuum sublimation (source temperature: 200 ºC under ~10^{-3} Pa) to give analytical sample of C_n-DNTT as a yellow solid.

47% isolated yield; yellow crystals from chlorobenzene; mp > 300ºC; ^{1}H NMR (270 MHz, CD_2Cl_2) δ 2.55 (s, 6H), 7.38 (d, 2H, J = 8.6 ArH), 7.72 (s, 2H, ArH), 7.94 (d, 2H, J = 8.6 Hz, ArH), 8.32 (s, 2H, ArH), 8.33 (s, 2H, ArH); IR (KBr) ν = 1447, 1373, 1273, 874 cm^{-1}; EI-MS, m/z = 368 (M^+) Anal. Calcd for $C_{24}H_{16}S_2$: C, 78.22; H, 4.38%. Found: C, 78.15; H, 4.09%.

3,10-Dimethyldinaphtho[2,3-*b*:2',3'-*f*]thieno[3,2-*b*]thiophen (3,10-DMDNTT)

The title compound was obtained in the same manner as that for 6-methyl isomer from 7-methyl--3-methylthio-2-naphthaldehyde.

52% isolated yield; yellow crystals from o-dichlorobenzene; mp > 300ºC; ^{1}H NMR (270 MHz, CD_2Cl_2) δ 2.58 (s, 6H), 7.37 (d, 2H, J = 9.2 Hz, ArH), 7.80 (s, 2H, ArH), 7.86 (d, 2H, J = 9.2 Hz, ArH), 8.28 (s, 2H, ArH), 8.38 (s, 2H, ArH); IR (KBr) ν = 1379, 1274, 880, 802 cm^{-1};.EI-MS, m/z = 368 (M^+). Anal. Calcd for $C_{24}H_{16}S_2$: C, 78.22; H, 4.38%. Found: C, 77.91; H, 4.12%.

2. Physicochemical properties of DMDNTTs

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). From the onsets of the oxidation peaks in Fig. S1, the HOMO level of these compounds are roughly estimated to be –5.3 eV for 2,9-DMDNTT and –5.35 eV for 3,10-DMDNTT under the premise that the energy level of Fc/Fc^+ is 4.8 eV below the vacuum level.[S2] UV-vis spectra in THF solution or thin films were recorded on a Shimadzu UV-3100 spectrometer.

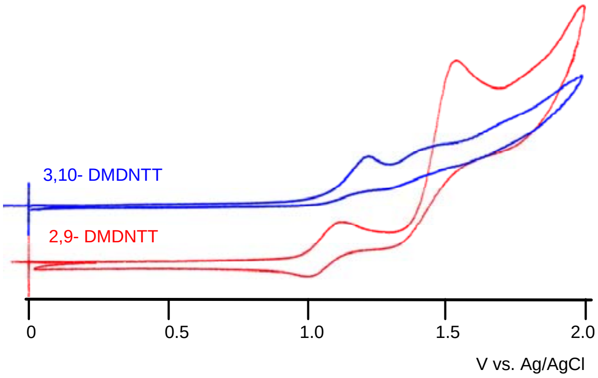


Fig. S1 Cyclic voltammograms of DMDNTTs.

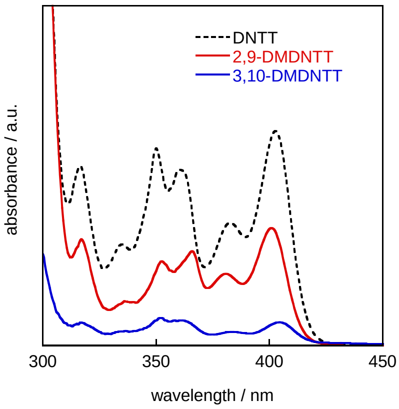


Fig. S2 UV-vis spectra of DNTT, 2,9-DMDNTT and 3,10-DMDNTT.

3. Structural characterization of DMDNTTs

Single crystal X-ray Analysis: Single crystals were obtained by thermal sublimation.[S3] The X-ray crystal structure analysis was made on a Rigaku MSC Mercury CCD (MoKα radiation, λ = 0.71070 Å, graphite monochromator, T = 293 K, 2θmax = 55.0°). The structure was solved by the direct method SHELXS-97. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. All calculations were performed using the SHELXL-97 package program.[S4]

Crystal data for 2,9-DMDNTT: $C_{24}H_{16}S_2$, M = 368.49, yellow plate, 0.40×0.25×0.02 mm^3, *Monoclinic*, space group $P2_1$ (no. 4), a = 11.686(12), b = 7.737(7), c = 10.674(11) Å, β = 114.187(5) °, V = 880.4(15) $Å^3$, Z = 2, D_{calc} = 1.390 gcm^{-3}, R = 0.0731 for 1949 observed reflections

(I > 2σ(I)) and 235 variable parameters, $R_w = 0.1929$ for all data (3857).

Crystal data for 3,10-DMDNTT: $C_{24}H_{16}S_2$, $M = 368.49$, yellow plate, 0.50×0.30×0.15 mm^3, *Monoclinic*, space group $P2_1/c$ (no. 14), $a = 6.148(2)$, b = 7.535(3), c = 18.559(7) Å, $b = 97.924(1)$ °, $V = 851.5(5)$ $Å^3$,, $Z = 2$, $D_{calc} = 1.437$ gcm^{-3}, $R = 0.0395$ for 1469 observed reflections (I > 2σ(I)) and 118 variable parameters, $R_w = 0.115$ for all data (1839).

Out-of-plane and in-plane XRDs of evaporated thin films: X-ray diffractions of thin films deposited on the Si/SiO_2 substrate were obtained with a Rigaku Ultima IV diffractometer with a Cu *K*α source (λ = 1.541 Å) in the air.

4. Device fabrication and evaluation

The Si/SiO_2 substrates (heavily doped n^+-Si (100)) were immersed in 1 mM OTS in toluene at 60 ºC for 20 mins to prepared OTS-modified substrates.[S5] OTFTs were fabricated in a “top-contact” configuration on the OTS-SAM modified Si/SiO_2 substrates with 200-nm-thick thermally grown SiO_2 (C_i = 17.3 nF cm^{-2}). A thin film (50 nm thick) of DMDNTTs as the active layer was vacuum-deposited on the 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 with various channel lengths (L = 40, 90, 140, and 190 μm) and width (W = 1500 μm). The characteristics of the OFET devices were measured at room temperature in air with a Keithley 4200 semiconducting parameter analyzer. Field-effect mobility (μ_{FET}) was calculated in the saturation regime (V_d = –60 V) of the I_d using the following equation,

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

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 ten different devices.

Table S1. Properties of DMDNTT-based TFTs[a].

	2,9-DMDNTT			3,10-DMDNTT		
L / μm	V_{th} / V	μ [b] / $cm^2\,V^{-1}\,s^{-1}$	$I_{on/off}$ [c]	V_{th} / V	μ [b] / $cm^2\,V^{-1}\,s^{-1}$	$I_{on/off}$ [c]
40	–2.6	0.39	10^8	–4.4	0.79	10^8
90	–3.0	0.33	10^7	–3.6	0.72	10^7
140	–3.2	0.33	10^7	–3.5	0.73	10^8
190	–3.0	0.35	10^7	–3.4	0.75	10^8

[a] fabricated on OTS-treated Si/SiO_2 substrates at 60 ºC during deposition. [b] extracted from the saturation regime (V_d =V_g = –60 V). [c] determined from transfer characteristics at V_g = –60 V.

5. Theoretical calculations

Molecular orbital calculation: All the calculations were performed with Gaussian 03 programs.[S6] Geometry optimization and normal mode MO calculations of DNTT and DMDNTTs were carried out by the DFT method at the B3LYP–6-31G(d) level.

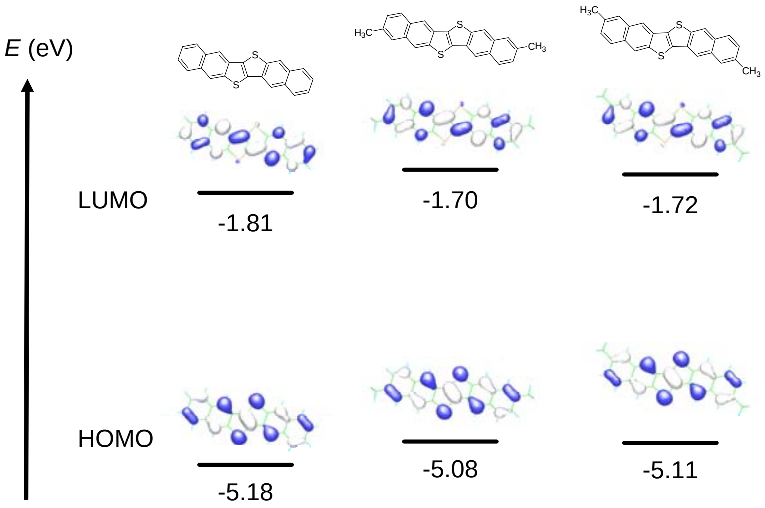


Fig. S3. Calculated HOMO and LUMO of DNTT, 2,9-DMDNTT and 3,10-DMDNTT.

Intermolecular transfer integrals of HOMOs: The transfer integrals (t) for neighboring molecules in the crystal structures were calculated using the fragment analysis method embedded in Amsterdam Differential Functional (ADF) program with the PW91 functional and Slater-type triple-ζ plus polarization (TZP) basis sets, following the procedure described by Siebbeles *et al.*[S7] and Chao *et al.*[S8]

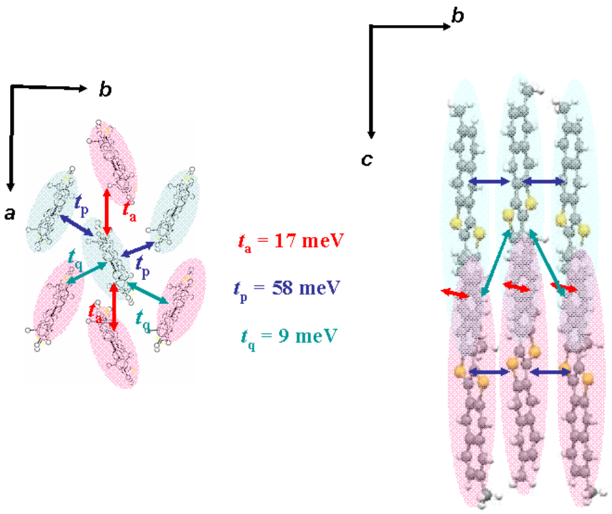


Fig. S4. Calculated intermolecular transfer integrals (t) between HOMOs in 2,9-DMDNTT crystals.

6. References

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