

*Electronic Supplementary Information (ESI) for*

**Packing structures of (trialkylsilyl)ethynyl-substituted dinaphtho[2,3-*b*:2',3'-*f*]thieno[3,2-*b*]thiophenes (DNTTs): effects of substituents on crystal structures and transport properties**

Kazuo Takimiya<sup>\*a,b,c</sup>, Sayaka Usui<sup>a</sup>, Aoi Sato<sup>a</sup>, Kiseki Kanazawa<sup>a,b</sup>, Kohsuke Kawabata<sup>a,b</sup>

<sup>a</sup>Department of Chemistry, Graduate School of Science, Tohoku University, 6-3 Aoba, Aramaki, Aoba-ku, Sendai, Miyagi 980-8578, Japan

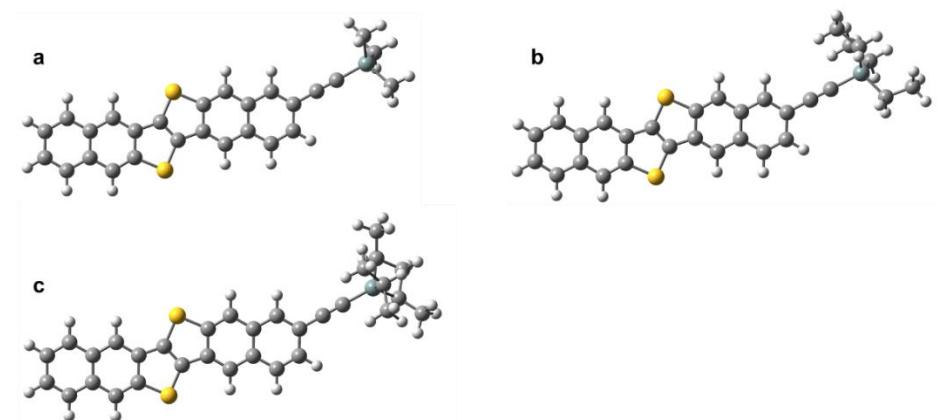
<sup>b</sup>RIKEN Center for Emergent Matter Science (CEMS), 2-1 Hirosawa, Wako, Saitama 351-0198, Japan

<sup>c</sup> Advanced Institute for Materials Research, Tohoku University (WPI-AIMR), 2-1-1 Katahira, Aoba-ku, Sendai, Miyagi 980-8577, Japan

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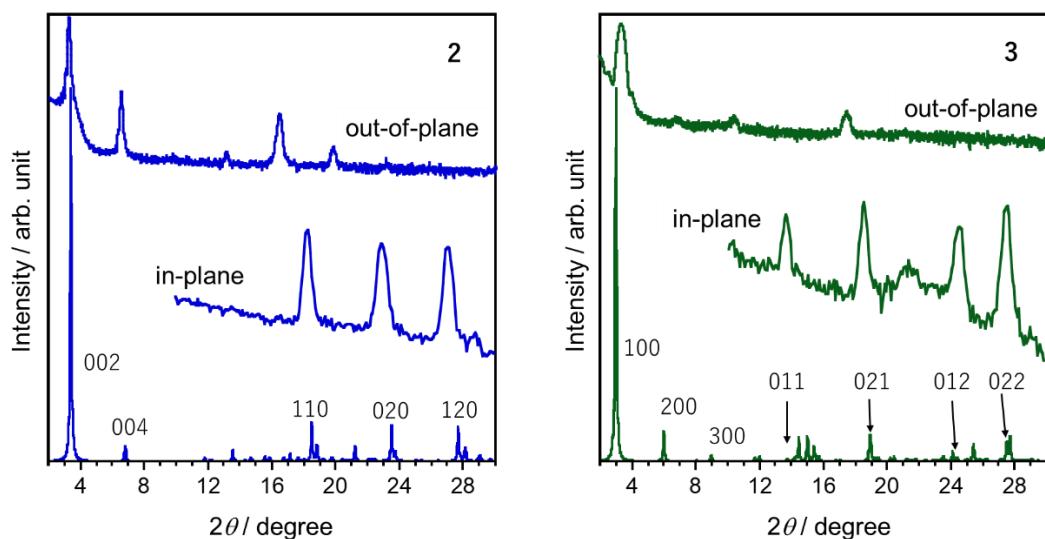
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## 1. Simulated molecular structures of 1–3



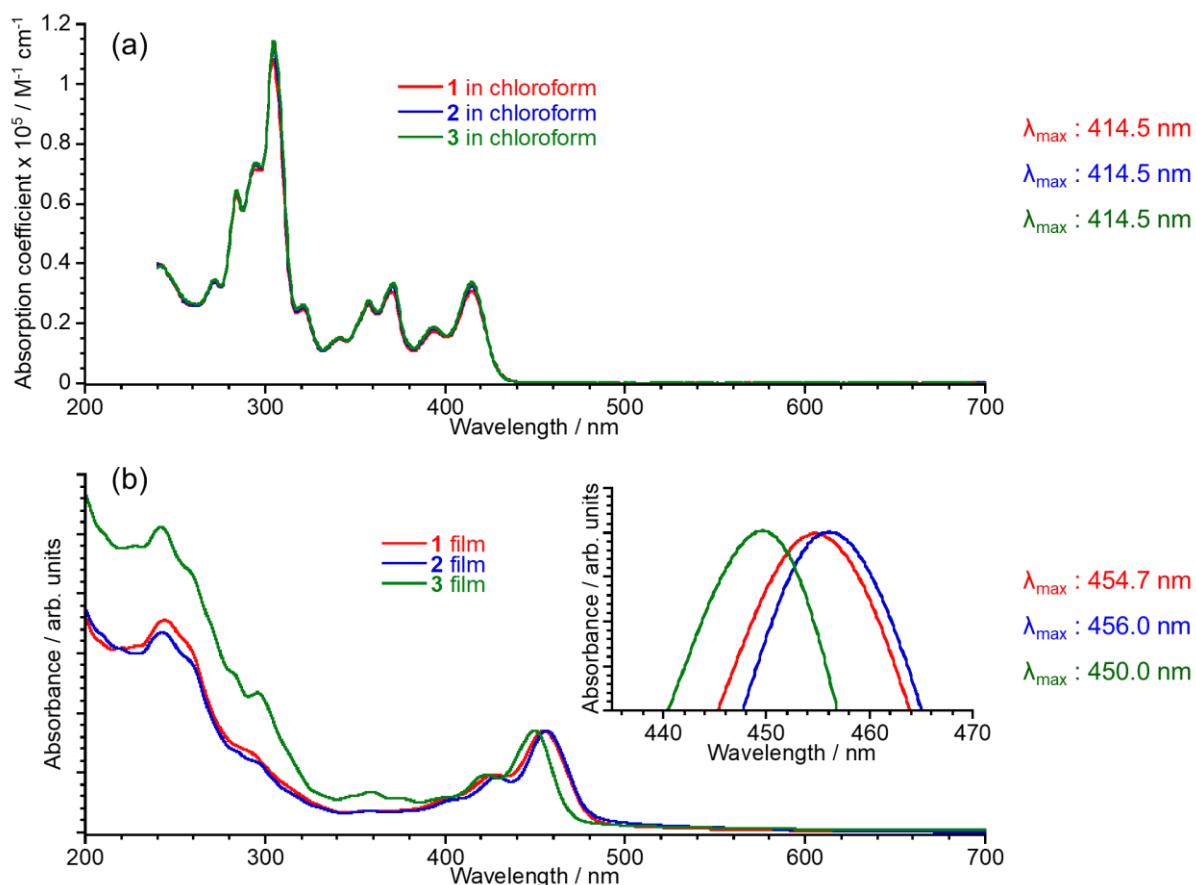
**Fig. S1.** Molecular structures of 1–3 (a–c, respectively) optimized with the DFT calculations (B3LYP/6-31G(d) level).

## 2. Simulated powder patterns and empirical XRD patterns of 2 and 3



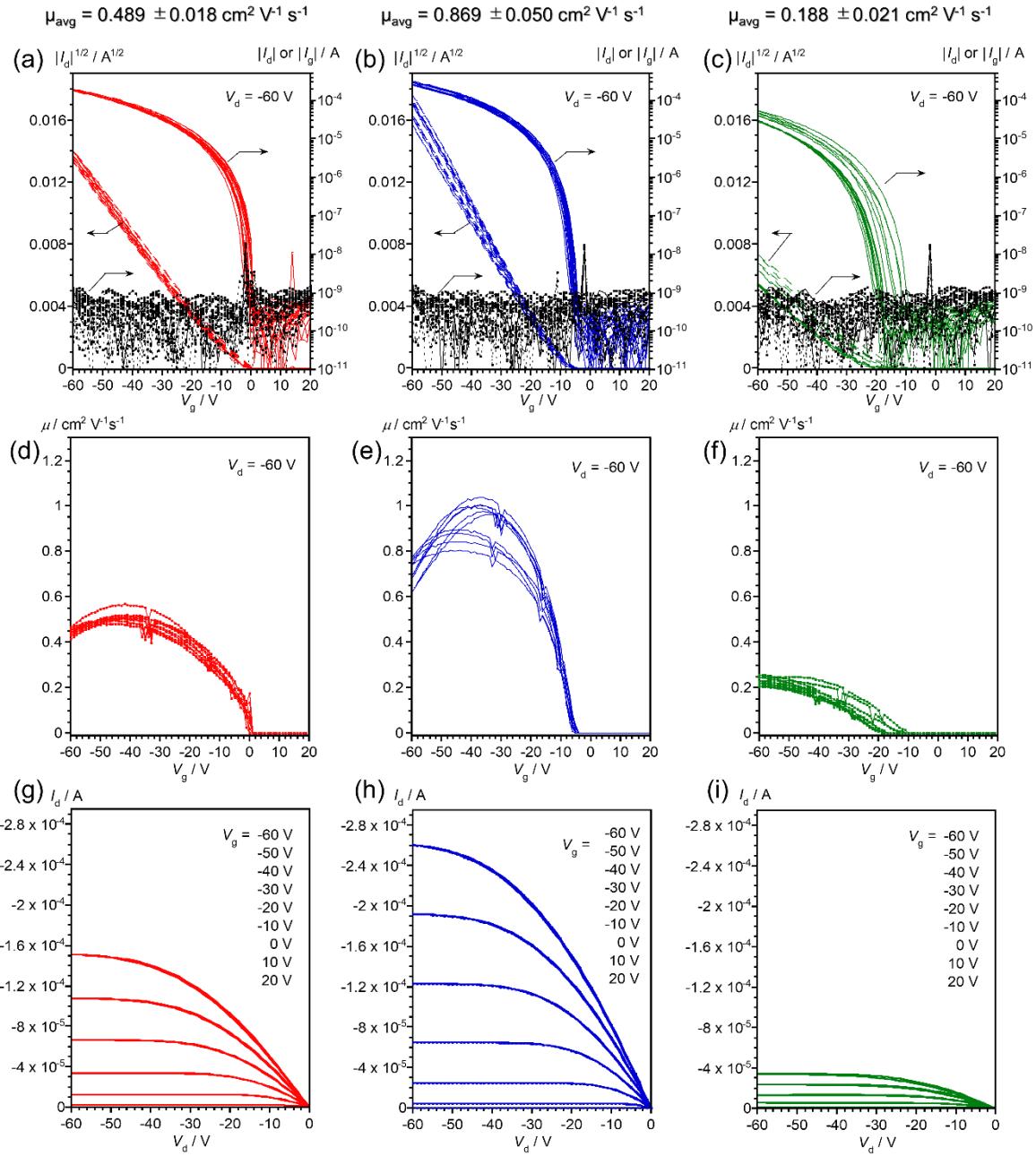
**Fig. S2.** Simulated powder patterns and empirical XRD data of 2 and 3.

### 3. UV-vis absorption spectra of **1–3**

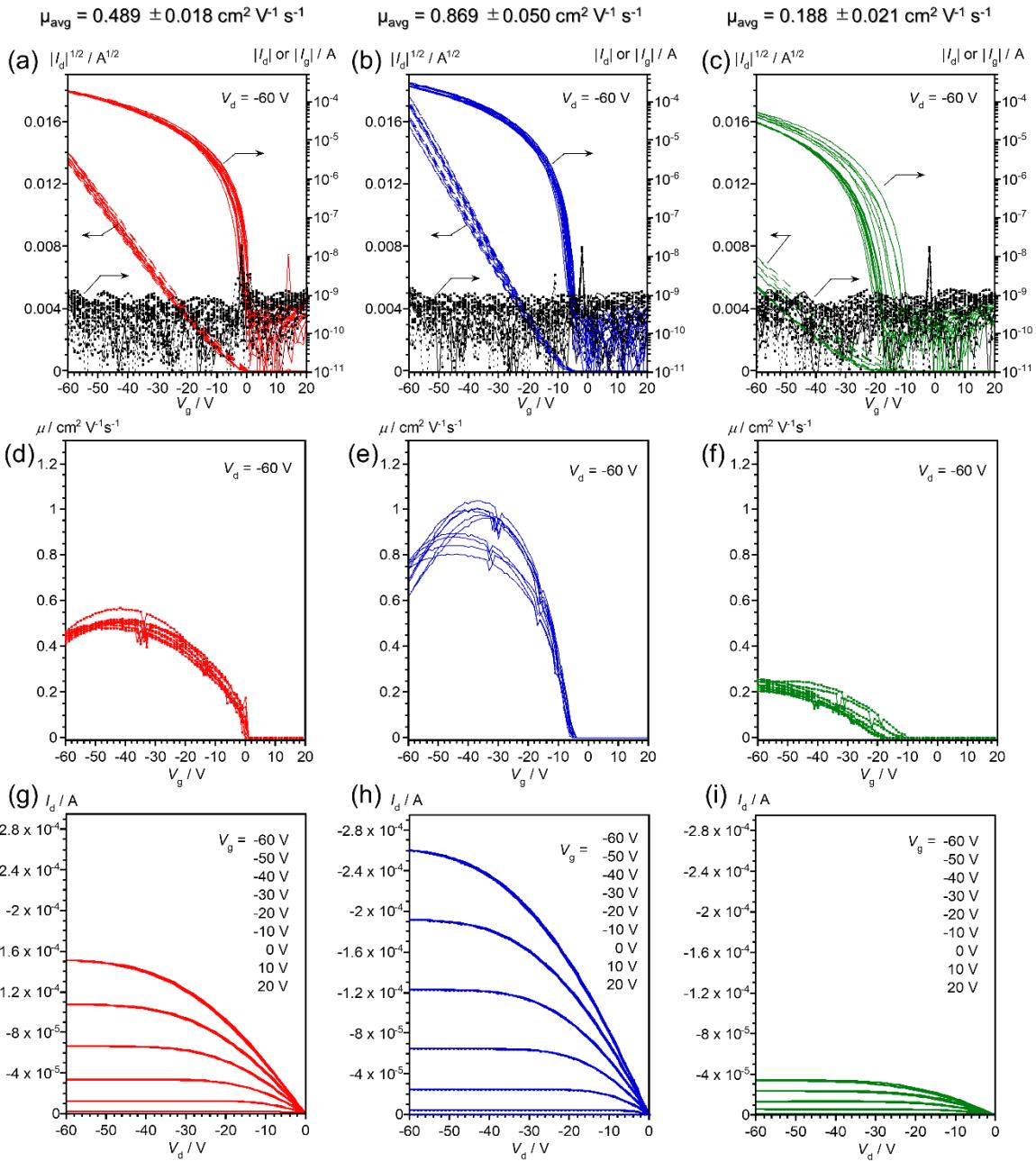


**Fig. S3.** UV-vis absorption spectra of **1–3** in chloroform solution (a) and in the thin-film state (b). Note that all the absorption spectra in solution are completely overlapped. In contrast, the thin-film absorption spectra of **1** and **2** are almost identical, whereas that of **3** shows characteristics blue shift.

#### 4. Characteristics of 1–3-based OFETs



**Fig. S4.** Statistic data of FET devices of 1- (a, d, g), 2- (b, e, h), and 3-based OFETs with the Au/MoO<sub>3</sub> source and drain electrodes (c, f, i) with vapor-deposited thin-films as the active layers. Transfer characteristics (a-c), mobility depending on the gate voltage (d-f), and output characteristics (g-i). The dotted lines in a-c are the gate leakage current.



**Fig. S5.** FET characteristics of 1- (a, d, g), 2- (b, e, h), and 3-based OFETs with gold source and drain electrodes (c, f, i) with vapor-deposited thin-films as the active layers. Transfer characteristics (a-c), mobility depending on the gate voltage (d-f), and output characteristics (g-i).

## 5. Partitioned intermolecular interaction energies in the solid state of 2 and 3

Table S1. Partitioned intermolecular interaction energy ( $E_{\text{intS}}$  / kcal mol $^{-1}$ ) of the molecular pairs in the packing structure of 2.

A	B	$E_{\text{elst}}^{\text{b}}$	$E_{\text{exch}}^{\text{b}}$	$E_{\text{indAB}}^{\text{b}}$	$E_{\text{indBA}}^{\text{b}}$	$E_{\text{disp}}^{\text{b}}$	$E_{\text{total}}^{\text{b}}$
DNTT	DNTT	-6.60	14.50	-0.41	-1.13	-22.25	-15.91
DNTT	TESE	-0.28	0.00	-0.01	0.03	-0.39	-0.711
TESE	DNTT	-0.19	0.32	0.05	-0.06	-1.48	-1.36
TESE	TESE	0.01	-0.00	0.00	-0.00	-0.00	0.01
All	All	-7.06	14.82	-0.39	-1.23	-24.12	-17.98

A	$B_{100}$	$E_{\text{elst}}^{\text{b}}$	$E_{\text{exch}}^{\text{b}}$	$E_{\text{indAB}}^{\text{b}}$	$E_{\text{indBA}}^{\text{b}}$	$E_{\text{disp}}^{\text{b}}$	$E_{\text{total}}^{\text{b}}$
DNTT	DNTT	-7.21	14.94	-1.13	-0.56	-23.01	-16.97
DNTT	TESE	-0.27	0.97	-0.05	0.07	-2.19	-1.48
TESE	DNTT	-0.32	1.07	-0.10	-0.10	-2.88	-2.33
TESE	TESE	0.01	0.00	0.00	0.00	-0.00	0.01
All	All	-7.78	16.98	-1.29	-0.60	-28.08	-20.77

A	$A_{100}$	$E_{\text{elst}}^{\text{b}}$	$E_{\text{exch}}^{\text{b}}$	$E_{\text{indAB}}^{\text{b}}$	$E_{\text{indBA}}^{\text{b}}$	$E_{\text{disp}}^{\text{b}}$	$E_{\text{total}}^{\text{b}}$
DNTT	DNTT	-6.43	11.05	-0.72	-0.69	-13.44	-10.22
DNTT	TESE	-0.07	0.00	-0.03	0.00	-0.20	-0.29
TESE	DNTT	-0.11	0.16	0.03	0.00	-0.89	-0.81
TESE	TESE	-0.85	3.59	-0.22	-0.05	-4.04	-1.57
All	All	-7.46	14.81	-0.94	-0.73	-18.57	-12.90

B	$B_{010}$	$E_{\text{elst}}^{\text{b}}$	$E_{\text{exch}}^{\text{b}}$	$E_{\text{indAB}}^{\text{b}}$	$E_{\text{indBA}}^{\text{b}}$	$E_{\text{disp}}^{\text{b}}$	$E_{\text{total}}^{\text{b}}$
DNTT	DNTT	0.34	0.00	-0.03	-0.03	-1.17	-0.89
DNTT	TESE	-0.14	0.00	0.00	0.01	-0.09	-0.22
TESE	DNTT	-0.10	0.00	0.00	-0.01	-0.17	-0.27
TESE	TESE	-0.05	0.66	-0.01	-0.02	-1.32	-0.74
All	All	0.06	0.66	-0.04	-0.05	-2.74	-2.12

(continued)

B	$B_{II0}$	$E_{\text{elst}}^{\text{b}}$	$E_{\text{exch}}^{\text{b}}$	$E_{\text{indAB}}^{\text{b}}$	$E_{\text{indBA}}^{\text{b}}$	$E_{\text{disp}}^{\text{b}}$	$E_{\text{total}}^{\text{b}}$
DNTT	DNTT	0.24	0.00	-0.01	-0.01	-0.28	-0.05
DNTT	TESE	-0.04	0.00	0.00	0.00	-0.05	-0.09
TESE	DNTT	-0.07	0.00	0.00	0.00	-0.04	-0.11
TESE	TESE	0.02	0.11	0.00	0.00	-0.39	-0.27
All	All	0.14	0.11	-0.01	-0.01	-0.76	-0.52

$B_{010}$	$B_{100}$	$E_{\text{elst}}^{\text{b}}$	$E_{\text{exch}}^{\text{b}}$	$E_{\text{indAB}}^{\text{b}}$	$E_{\text{indBA}}^{\text{b}}$	$E_{\text{disp}}^{\text{b}}$	$E_{\text{total}}^{\text{b}}$
DNTT	DNTT	-0.03	0.00	0.00	0.00	-0.54	-0.58
DNTT	TESE	-0.03	0.00	0.00	0.00	-0.07	-0.10
TESE	DNTT	-0.03	0.00	0.00	0.00	-0.03	-0.06
TESE	TESE	0.03	0.00	0.00	0.00	-0.09	-0.06
All	All	-0.05	0.00	0.00	0.00	-0.73	-0.79

<sup>a</sup> Refer Fig. 4b for the definition of the molecular pair. <sup>b</sup>  $E_{\text{elst}}$ : electrostatic interaction energy,  $E_{\text{exch}}$ : exchange interaction energy,  $E_{\text{indAB}}$ : induction interaction energy,  $E_{\text{indBA}}$ : induction interaction energy,  $E_{\text{disp}}$ : dispersion energy,  $E_{\text{total}}$ : the sum of each energetic terms. <sup>c</sup>  $E_{\text{int}}$  separately calculated by SAPT0.

Table S2. Partitioned intermolecular interaction energy ( $E_{\text{intS}} / \text{kcal mol}^{-1}$ ) of the molecular pairs in the packing structure of **3**.

A	A'	$E_{\text{elst}}^{\text{b}}$	$E_{\text{exch}}^{\text{b}}$	$E_{\text{indAB}}^{\text{b}}$	$E_{\text{indBA}}^{\text{b}}$	$E_{\text{disp}}^{\text{b}}$	$E_{\text{total}}^{\text{b}}$
DNTT	DNTT	-13.68	38.36	-1.58	-1.58	-48.34	-26.82
DNTT	TIPSE	-0.50	0.01	-0.02	0.15	-0.49	-0.85
TIPSE	DNTT	-0.45	0.01	0.15	-0.02	-0.49	-0.85
TIPSE	TIPSE	0.01	0.00	0.00	0.00	0.00	0.01
All	All	-14.67	38.38	-1.45	-1.45	-49.32	-28.51

A	$A'_{001}$	$E_{\text{elst}}^{\text{b}}$	$E_{\text{exch}}^{\text{b}}$	$E_{\text{indAB}}^{\text{b}}$	$E_{\text{indBA}}^{\text{b}}$	$E_{\text{disp}}^{\text{b}}$	$E_{\text{total}}^{\text{b}}$
DNTT	DNTT	-8.72	15.49	-0.89	-0.89	-16.38	-11.40
DNTT	TIPSE	-0.34	1.10	-0.11	-0.01	-2.16	-1.52
TIPSE	DNTT	-0.34	1.10	-0.01	-0.11	-2.16	-1.51
TIPSE	TIPSE	0.00	0.00	0.00	0.00	0.00	0.00
All	All	-9.39	17.69	-1.01	-1.01	-20.71	-14.43

(continued)

A	B'	$E_{\text{elst}}^{\text{b}}$	$E_{\text{exch}}^{\text{b}}$	$E_{\text{indAB}}^{\text{b}}$	$E_{\text{indBA}}^{\text{b}}$	$E_{\text{disp}}^{\text{b}}$	$E_{\text{total}}^{\text{b}}$
DNTT	DNTT	-2.35	.6218.69	-0.44	-0.63	-10.97	-5.70
DNTT	TIPSE	0.06	0.00	0.01	0.00	-0.15	-0.08
TIPSE	DNTT	-0.27	0.05	-0.02	-0.02	-0.59	-0.85
TIPSE	TIPSE	0.01	0.00	0.00	0.00	0.00	0.01
All	All	-2.54	8.74	-0.45	-0.65	-11.71	-6.62

A	$B_{010}$	$E_{\text{elst}}^{\text{b}}$	$E_{\text{exch}}^{\text{b}}$	$E_{\text{indAB}}^{\text{b}}$	$E_{\text{indBA}}^{\text{b}}$	$E_{\text{disp}}^{\text{b}}$	$E_{\text{total}}^{\text{b}}$
DNTT	DNTT	-6.38	13.15	-1.23	-0.51	-19.92	-14.88
DNTT	TIPSE	-0.51	0.00	-0.05	-0.01	-0.17	-0.74
TIPSE	DNTT	-0.09	0.39	-0.01	0.06	-1.71	-1.36
TIPSE	TIPSE	-0.34	2.46	-0.10	-0.04	-3.89	-1.92
All	All	-7.33	16.00	-1.40	-0.49	-25.68	-18.90

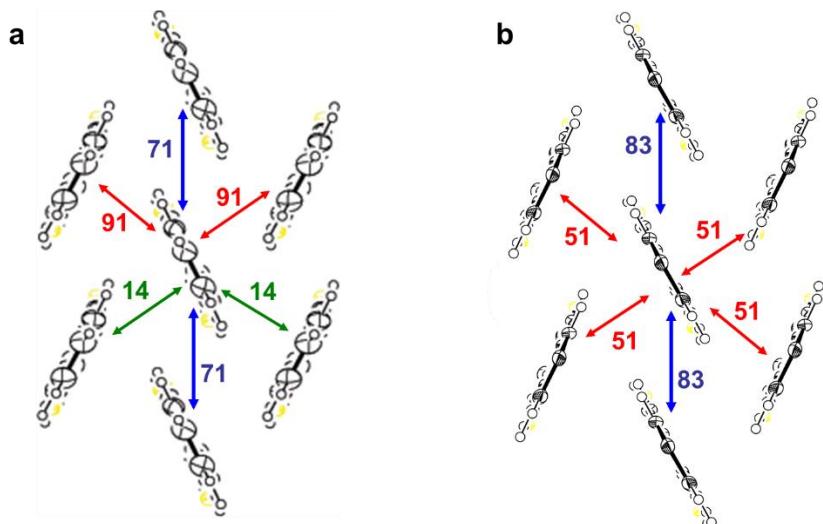
(continued)

A	$A_{001}$	$E_{\text{elst}}^{\text{b}}$	$E_{\text{exch}}^{\text{b}}$	$E_{\text{indAB}}^{\text{b}}$	$E_{\text{indBA}}^{\text{b}}$	$E_{\text{disp}}^{\text{b}}$	$E_{\text{total}}^{\text{b}}$
DNTT	DNTT	-0.02	0.00	-0.04	-0.04	-1.31	-1.40
DNTT	TIPSE	-0.12	0.00	0.00	0.01	-0.05	-0.17
TIPSE	DNTT	-0.01	0.24	0.00	-0.01	-1.22	-0.99
TIPSE	TIPSE	-0.28	0.83	-0.01	-0.04	-2.10	-1.59
All	All	-0.42	1.08	-0.04	-0.09	-4.68	-4.15

A	B	$E_{\text{elst}}^{\text{b}}$	$E_{\text{exch}}^{\text{b}}$	$E_{\text{indAB}}^{\text{b}}$	$E_{\text{indBA}}^{\text{b}}$	$E_{\text{disp}}^{\text{b}}$	$E_{\text{total}}^{\text{b}}$
DNTT	DNTT	0.06	0.00	-0.01	-0.03	-0.62	-0.59
DNTT	TIPSE	-0.01	0.00	0.00	-0.01	-0.33	-0.35
TIPSE	DNTT	-0.05	0.00	-0.01	0.01	-0.08	-0.13
TIPSE	TIPSE	-0.54	2.13	-0.04	-0.10	-4.17	-2.72
All	All	-0.54	2.14	-0.05	-0.13	-5.20	-3.78

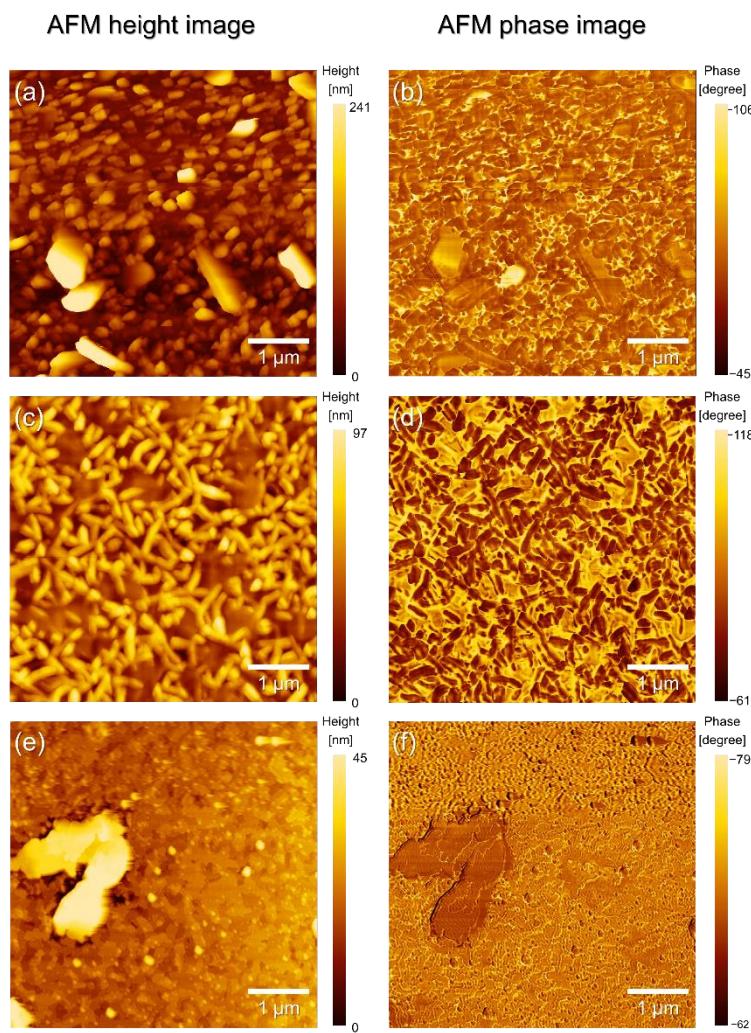
<sup>a</sup> Refer Fig. 4e for the definition of the molecular pair. <sup>b</sup>  $E_{\text{elst}}$ : electrostatic interaction energy,  $E_{\text{exch}}$ : exchange interaction energy,  $E_{\text{indAB}}$ : induction interaction energy,  $E_{\text{indBA}}$ : induction interaction energy,  $E_{\text{disp}}$ : dispersion energy,  $E_{\text{total}}$ : the sum of each energetic terms. <sup>c</sup>  $E_{\text{int}}$  separately calculated by SAPTO.

## 6. Distribution of transfer integrals of parent and C<sub>10</sub>-DNTT in the solid state



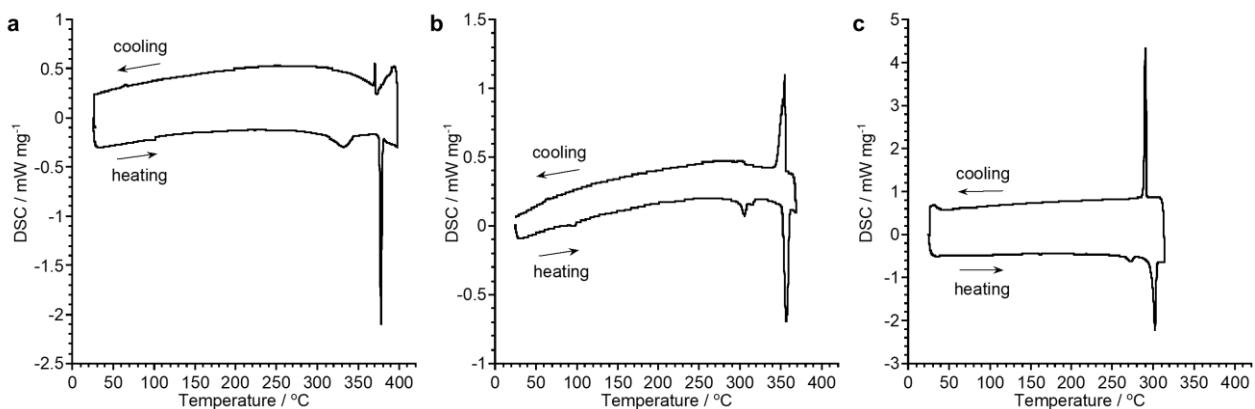
**Fig. S6.** Calculated transfer integrals ( $ts$ , meV) of parent DNTT (a) and 2,9-didecyl-DNTT (b). Note that decyl groups of 2,9-didecyl-DNTT were omitted for clarity. The maximum  $t$  in DNTT is larger than that in 2,9-didecyl-DNTT, but the latter has a more balanced distribution of  $ts$ .

## 7. AFM images of vapor deposited thin-films of 1–3



**Fig. S7.** AFM images of vapor deposited thin films of **1** (a, b), **2** (c, d), and **3** (e, f).

## 8. DSC traces of 1–3



**Fig. S8.** DSC traces of **1** (a), **2** (b), and **3** (c).