Electronic Supplementary Information (ESI)

# Self-assembled structures of bent-shaped $\pi$ -conjugated compounds:

# Effect of siloxane groups for nano-segregation

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#### S.1. General methods

All <sup>1</sup>H- and <sup>13</sup>C-NMR spectra were performed in CDCl<sub>3</sub> solution on a Varian UNITY INOVA400NB spectrometer. The High-Resolution Mass Spectrometry (HRMS) measurements were carried out by using a BRUKER microTOF II. FT-IR measurements were carried out on a BRUKER FT-IR ALPHA II spectrometer by using the solid film on a silicon substrate. The Karstedt's catalyst and 1,1,1,3,3-pentamethyldisiloxane were purchased from Gelest Inc. Other reagents were purchased from Tokyo Chemical Industry, Kanto Chemicals, and Wako Pure Chemical Industries. All reagents were used without further purification. All reactions were performed under argon atmosphere in a well-dried flask equipped with a magnetic stirring bar.

#### S.2. Synthesis of materials

The alkenylthienylboric acid ester **3** was synthesized by the similar conditions of analogous compounds previously reported.<sup>\$1,\$2</sup> The intermediate compound **4** was synthesized via the Suzuki-Miyaura reaction between 1,3-dibromo-5-fluorobenzene and 2-thienylboric acid ester. The bromination reaction of compound **4** with using *N*-bromosuccinimide was afforded to dibrominated compound **5**.



**Scheme S1** Synthetic route of intermediated compounds.

#### 2-(7-Octenyl)thienylboric acid 2,2-dimethyl-1,3-propanediyl ester (3)

To a solution of 2-(7-octenyl)thiophene (10.0 g, 51.5 mmol) in dry THF (200 mL) was slowly added *n*-BuLi (1.6 M in *n*-hexane soln., 37.5 mL, 60.0 mmol) with dry THF (10 mL) at -78 °C. After the addition of *n*-BuLi, the mixture was stirred for 1 h at -78 °C. Then, the mixture was allowed to warm to 0 °C for 10 min and cooled down to -78 °C again. Trimethyl borate (7.0 mL, 62.7 mmol) was slowly dropwised over 20 min. to reactant mixture at -78 °C. The obtained pale-yellow suspension was gradually warmed to room temperature and stirred for 20 h. Then, 2,2-dimethylpropanediol (6.45 g, 62.0 mmol) with dry THF (30 mL) was added to the orange reactant mixture at 0 °C. The mixture was warmed to room temperature and stirred for 4.5 h. After the addition of H<sub>2</sub>O (20 mL), the product was separated and washed with sat.NH<sub>4</sub>Cl aq. (100 mL), brine (100 mL) and H<sub>2</sub>O (100 mL) in this order. The aqueous layer was extracted with ethyl acetate (100 mL ×1, 50 mL ×2). The collected organic fractions were combined and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After filtration and evaporation, the crude solution was purified by the silica gel column chromatography (eluent: *n*-hexane  $\rightarrow n$ -hexane/ethyl acetate = 10/1; v/v, gradient) and dried *in vacuo* to give 2-(7-octenyl)thienylboric acid 2,2-dimethyl-1,3-propanediyl ester (**3**) as a colourless solid (11.0 g, 70 % yield).

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  [ppm] = 7.39 (d, 1H, *J* = 3.2 Hz), 6.83 (d, 1H, *J* = 3.2 Hz), 5.81 (ddt, 1H, *J* = 17.2, 10.4, 6.8 Hz), 4.99 (ddd, 1H, *J* = 17.2, 3.6, 1.6 Hz), 4.93 (ddt, 1H, *J* = 10.4, 2.2, 1.2 Hz), 3.74 (s, 4H), 2.83 (t, 2H, *J* = 7.6 Hz), 2.03 (quartet, 2H, *J* = 7.0 Hz), 1.67 (quintet, 2H, *J* = 7.6 Hz), 1.42-1.22 (m, 6H), 1.02 (s, 6H); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  [ppm] = 152.6, 139.2, 135.8, 125.7, 114.1, 72.3, 33.8, 32.0, 31.7, 30.2, 29.4, 29.3, 29.1, 28.9, 21.9; HRMS (APCI-ESI): molecular weight: 306.2710 (C<sub>17</sub>H<sub>27</sub>BO<sub>2</sub>S); m/z calcd. for [C<sub>19</sub>H<sub>32</sub>BO<sub>2</sub>S]<sup>+</sup> : 335.2211 ([M+CH<sub>2</sub>CH<sub>3</sub>]<sup>+</sup>); found 335.2235.

#### 1,3-bis(2-thienyl)-5-fluorobenzene (4)

To a stirred solution of 1,3-dibromo-5-fluorobenzene (3.07 g, 12.1 mmol), 2-thienylboronic acid (4.54 g, 35.5 mmol) and tetrakis(triphenylphosphine)palladium(0) (Pd(PPh<sub>3</sub>)<sub>4</sub>, 1.23 g, 1.06 mmol) in 1,2-dimethoxyethane (250 mL) was added Na<sub>2</sub>CO<sub>3</sub> aqueous solution (180 mL, 0.35 mol). After the reaction mixture was stirred under reflux for 11 h, the mixture was cooled down to room temperature. After the addition of H<sub>2</sub>O (150 mL), the product was extracted with tetrahydrofuran (250 mL ×1). The aqueous layer was extracted with *n*-hexane (100 mL ×3). The collected organic fractions were combined and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After filtration and evaporation, the crude product was purified by silica gel column chromatography (eluent: *n*-hexane/toluene = 5/1; v/v). The product was recrystallized from ethanol and dried *in vacuo* to give 3,5-bis(2-thienyl)fluorobenzene (**4**) as a white crystal (2.75 g, 88 % yield).

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  [ppm] = 7.60 (t, 1H, *J* = 1.6 Hz), 7.36 (dd, 2H, *J* = 3.6, 1.2 Hz), 7.33 (dd, 2H, *J* = 5.2, 1.2 Hz), 7.21 (dd, 2H, *J* = 9.6, 1.6 Hz), 7.11 (dd, 2H, *J* = 5.2, 3.6 Hz); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  [ppm] = 163.3 (d, *J* = 245 Hz), 142.7 (d, *J* = 3 Hz), 136.9 (d, *J* = 9 Hz), 128.2, 125.7, 124.2, 119.2 (d, *J* = 3 Hz), 111.6 (d, *J* = 23 Hz); HRMS (APCI-ESI): molecular weight: 260.3444 (C<sub>14</sub>H<sub>9</sub>FS<sub>2</sub>); m/z calcd. for [C<sub>14</sub>H<sub>9</sub>FS<sub>2</sub>]<sup>+</sup> : 260.0124 (M<sup>+•</sup>); found 260.0142.

#### 1,3-bis(5-bromo-2-thienyl)-5-fluorobenzene (5)

To a solution of **4** (2.51 g, 9.62 mmol) in dry THF (70 mL) was slowly added *N*-bromosuccinimide (3.50 g, 19.6 mmol) at 0 °C. Then, the mixture was allowed to warm to room temperature and stirred for 20 h. After the addition of 4 wt% Na<sub>2</sub>CO<sub>3</sub> aqueous solution (90 mL), the product was extracted with toluene (50 mL ×4). The extract was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After filtration and evaporation, the crude product was purified by recrystallization from toluene/methanol. The colourless crystal was collected by filtration and dried *in vacuo* to afford 3,5-bis(5-bromo-2-thienyl)fluorobenzene (**5**) (3.13 g, 78 % yield).

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  [ppm] = 7.38 (t, 1H, *J* = 1.4 Hz), 7.12 (dd, 2H, *J* = 9.6, 1.4 Hz), 7.09 (d, 2H, *J* = 4.0 Hz), 7.06 (d, 2H, *J* = 4.0 Hz); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  [ppm] = 163.4 (d, *J* = 245 Hz), 143.7, 136.3 (d, *J* = 9 Hz), 131.0, 124.5, 118.5 (d, *J* = 2 Hz), 112.8, 111.7 (d, *J* = 23 Hz); HRMS (APCI-ESI): molecular weight: 418.1364 (C<sub>14</sub>H<sub>7</sub>Br<sub>2</sub>FS<sub>2</sub>); m/z calcd. for [C<sub>14</sub>H<sub>7</sub>Br<sub>2</sub>FS<sub>2</sub>]<sup>+</sup> : 417.8314 (M<sup>+•</sup>); found 417.8347.

#### S.3. Differential scanning calorimetry



**Fig. S1** DSC thermograms of (a) **1** and (b) **2**.

# S.4. Polarizing optical micrographs



**Fig. S2** POM images of **1** on air cooling process; (a) during the phase transition, (b) at 63 °C, (c) after aging at 63 °C, and (d) after cooling to room temperature from (c).



**Fig. S3** POM images of **2** (a) during the phase transition at room temperature, (b) after aging at room temperature.

### S.5. X-ray diffractions

Miller index ( <i>h k l</i> )	$2\theta$ / degree	<i>d /</i> nm
100	2.41	3.663
200	4.87	1.813
300	7.32	1.207
400	9.79	0.903
001	10.88	0.812
020	12.13	0.729
500	12.25	0.722
220	13.01	0.680
311	14.51	0.610
600	14.71	0.602
610	15.96	0.555
501	16.37	0.541
221	17.07	0.519
700	17.20	0.515
800	19.57	0.453
330	19.69	0.450
521	20.30	0.437
430	20.79	0.427
002	21.89	0.406
900	22.06	0.403
621	22.19	0.400
202	22.61	0.393
212	23.52	0.378
402	24.10	0.369
10 0 0	24.57	0.362

**Table S1** The index of X-ray diffraction peaks in the crystalline phase of **1** at 70 °C.

The lattice constant *a* is determined as the average value of  $d_{n00} \times n$  (n = 1, 2, 3, ...). The lattice constant *b* is estimated from the value of  $d_{020} \times 2$ . The average value of  $d_{00n} \times n$  (n = 1, 2) gives the lattice constant *c*.

The number of molecules in a unit cell (Z) can be determined by the following equation:

$$Z = \frac{\rho a b c N_A}{M_w} \qquad \text{(Eq. 1)}$$

In Eq. 1, *r*, *N*<sub>A</sub>, *M*<sub>w</sub> are the density, the Avogadro's constant, and the molecular weight, respectively. In the layered crystalline structure of **1** at 70 °C, the lattice constants are *a* = 3.62 nm, *b* = 1.46 nm, *c* = 0.81 nm. The value of Mw is 644.9844 g mol<sup>-1</sup> for **1**. Assuming  $\rho$  = 1.0 g cm<sup>-3</sup>, the value of *Z* is calculated to be 3.996 ≈ 4.



Fig. S4 The predicted crystal packing model of 1.

Table S2 The index of X-ray diffraction peaks in the crystalline phase of 2 at 29 °C.

Miller index ( <i>h k l</i> )	$2\theta$ / degree	<i>d /</i> nm
110	2.42	3.648
020	3.92	2.252
220	4.86	1.817
130	6.02	1.467
001	8.76	1.009
711	13.42	0.659
660	14.56	0.608
080	15.62	0.567
880	19.38	0.458
881	21.26	0.418
991	23.44	0.379

The lattice constant *b* is determined as the average value of  $d_{0n0} \times n$  (n = 2, 8). The value of  $d_{001}$  gives the lattice constant *c*. The lattice constant *a* is calculated to minimize the errors of each value of  $d_{hk0}$  and  $d_{hkl}$  (h, k, l = 1, 2, ...) by using the b = 4.54 nm, c = 1.01 nm. In the cylindrical crystalline structure of **2** at 29 °C, the lattice constants are a = 6.20 nm, b = 4.54 nm, c = 1.01 nm. The value of Mw is 941.6884 g mol<sup>-1</sup> for **2**. Assuming  $\rho = 1.0$  g cm<sup>-3</sup>, the value of *Z* is estimated to be 18.17  $\approx$  18 from Eq. 1.



**Fig. S5** The predicted crystal packing model of **2**.

### S.6. Atomic force microscopy



**Fig. S6** (a) AFM height image, (b) AFM phase image and (c) the cross-section trace of drop-casted sample of **2** in another position on the HOPG substrate.



**Fig. S7** (a) AFM height image and (b) AFM phase image of the drop-casted film of **2** after aging at room temperature.



Fig. S8 AFM phase image of drop-casted sample of 2 in another position on the HOPG substrate.



**Fig. S9** AFM phase image of drop-casted films prepared from the 0.005  $\mu$  solution of **1/2** in the other position.

### S.7. Phase transition behaviours of the equimolar mixture



**Fig. S10** The DSC thermogram of the binary mixture **1/2**.

S.8. <sup>1</sup>H- and <sup>13</sup>C-NMR spectroscopy

Compound 1





























Fig. S18 <sup>13</sup>C-NMR spectrum of compound 4.

# Compound 5









#### Notes and references

- S1 Y. Funatsu, A. Sonoda and M. Funahashi, J. Mater. Chem. C, 2015, 3, 1982.
- S2 A. Seki and M. Funahashi, *Chem. Lett.*, 2016, **45**, 616.