# **Supporting Information**

# Cofacial versus Coplanar Arrangement in Centrosymmetric Packing Dimers of Dipolar Small Molecules: Structural Effects on the Crystallization Behaviors and Optoelectronic Characteristics

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#### Instrumentation

**Molecular Characterization.** <sup>13</sup>C and <sup>1</sup>H NMR spectra were recorded in deuterochloroform (or other given solvents) as an internal reference using Varian Mercury Plus-400 spectrometer. High-resolution mass spectrometry was performed on a JMS-700 spectrometer in FAB mode. IR spectra were obtained on a Varian 640-IR. Melting points were determined on a Fargo MP-1D melting point apparatus. Elemental analyses were analyzed on an Elementar Vario EL-III analyzer.

UV/Visible Absorption Spectroscopy. UV/Vis absorption spectra in anhydrous  $CH_2Cl_2$  solutions were acquired with a Jasco V-670 spectrophotometer. Pristine 50-nm-thick thin-films were prepared by vacuum deposition onto ITO substrates and the absorption spectra were recorded on a Perkin Elmer. Films were annealed on a hot plate for 2 minutes at given temperatures and cooled to room temperature for absorption measurements (Figure 1b and c).

**Cyclic Voltammetry (CV).** The electrochemical properties were performed on a CH Instruments model CHI619B in a one-compartment three-electrode electrochemical cell equipped with a glassy carbon working electrode, a platinum wire counter electrode, and a Ag/AgCl reference electrode. Oxidation potentials were measured by cyclic voltammetry (CV) in anhydrous  $CH_2Cl_2$  (1.0 mM) with 0.1 M tetra-*n*-butylammonium hexafluorophosphate (TBAPF<sub>6</sub>) as a supporting electrolyte. All measurements were performed at a scan rate of 100 mV/s. All oxidation potentials reported were calibrated with the ferrocene/ferrocenium redox couple (Fc/Fc<sup>+</sup>) as internal standard. For each molecule, the oxidation potential ( $E_{ox}$ ) was obtained by halving the sum of two reversible oxidation peaks and the value mentioned herein was determined assuming the HOMO level of Fc/Fc<sup>+</sup> to be 4.8 eV.

#### **Synthetic Procedure and Details**

**Materials.** All reactants were reagent grades and purchased commercially without further purifications. Solvents for syntheses were freshly distilled according to standard procedures before used. All reactions were carried out under an atmosphere of nitrogen or argon. The starting materials ethyl 5-bromo-2-(thiophen-2-yl)benzoate (S1) and 6-bromo-4,4-di-*p*-tolyl-4*H*-indeno[1,2-*b*]thiophene (1b) were prepared as details reported in the literature.<sup>1</sup>



Scheme S1. Syntheses of building block 1a.

**5-Bromo-2-(thiophen-2-yl)benzoic acid (S2)**. To a stirred solution of **S1** (18 g, 57.8 mmol) in EtOH (200 mL) at room temperature was added an aqueous solution of 4 M NaOH (170 mL). The mixture was warmed and stirred at 100 °C for 1.5 h. The reaction mixture was then cooled to 0 °C before dropwise addition of concentrated HCl. After evaporation of EtOH, the crude was extracted with ethyl acetate/water, dried in vacuo and reprecipitated with hexane to obtain pure compound **S2** as a white solid (15.5 g, 95%). M. p. 156–157 °C ; IR (KBr) *v* 3090, 1688, 1443, 1300, 825, 718 cm<sup>-1</sup>; <sup>1</sup>H NMR (Acetone-*d*<sub>6</sub>, 400 MHz)  $\delta$  7.89 (d, *J* = 2.4 Hz, 1H), 7.74 (dd, *J* = 8.2, 2.2 Hz, 1H), 7.53 (dd, *J* = 4.8, 1.2 Hz, 1H), 7.47 (d, *J* = 8.4 Hz, 1H), 7.17 (dd, *J* = 3.4, 1.4 Hz, 1H), 7.09 (m, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$  172.1, 140.3, 134.9, 134.0, 133.3, 132.4, 131.7, 127.5, 127.2, 126.6, 121.7; HRMS (*m*/*z*, FAB<sup>+</sup>) calcd. for C<sub>11</sub>H<sub>7</sub><sup>79</sup>BrO<sub>2</sub>S 281.9350, C<sub>11</sub>H<sub>7</sub><sup>81</sup>BrO<sub>2</sub>S 283.9330; found 281.9357, 283.9339.

**6-Bromo-4***H***-indeno[1,2-***b***]thiophen-4-one (S3). Oxalyl chloride (320 mmol, 27.5 mL) was added to a mixture of acid S2 (16.5 g, 58.3 mmol) and anhydrous CH\_2Cl\_2 (150 mL) under N<sub>2</sub> atmosphere at room temperature. The reaction mixture was then added with few drops of anhydrous DMF and stirred overnight at room temperature. After removal of oxalyl chloride and CH\_2Cl\_2 under vacuum, a solution of SnCl<sub>4</sub> (9** 

mL) in anhydrous benzene (40 mL) was then slowly added to a solution of acid chloride in anhydrous benzene (80 mL) at 0 °C under N<sub>2</sub> atmosphere. After 0.5 h, the iced bath was removed and the reaction mixture was stirred for another 0.5 h at room temperature. The reaction mixture was poured into a mixture of ice (300 mL) and a 1 M aqueous solution of HCl (160 mL). The organic phase was extracted with ethyl acetate, washed with water, dried over MgSO<sub>4</sub>, and concentrated in vacuo. Target ketone **S3** was collected after silica chromatography (gradient eluent: ethyl acetate/hexane = 1/10 to pure CH<sub>2</sub>Cl<sub>2</sub>) as an orange solid (13.2 g, 85%). M. p. 172–173 °C; IR (KBr) v 3111, 3076, 1713, 1599, 1446, 1408, 1257, 1212, 1149, 817, 742 cm<sup>-1</sup>; <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 400 MHz)  $\delta$  7.49 (m, 2H), 7.25 (d, *J* = 4.8 Hz, 1H), 7.1 (d, *J* = 4.8 Hz, 1H), 7.04 (d, *J* = 7.6 Hz, 1H); <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, 100 MHz)  $\delta$  185.6, 158.6, 142.3, 138.4, 137.8, 136.6, 130.5, 127.1, 122.4, 121.6, 121.1; HRMS (*m/z*, FAB<sup>+</sup>) calcd. for C<sub>11</sub>H<sub>5</sub><sup>79</sup>BrOS 263.9244, C<sub>11</sub>H<sub>5</sub><sup>81</sup>BrOS 265.9224; found 263.9237, 265.9219.

**6-Bromo-4***H***-indeno[1,2-***b***]thiophene (S4). A mixture of ketone S3 (13.2 g, 49.8 mmol), hydrazine (64%, 13.5 mL) and diethylene glycol (250 mL) was stirred at 80 °C for 1 h and refluxed for another 1 h. An aqueous solution (60 mL) of potassium hydroxide (14 g, 249 mmol) was added slowly to the reaction mixture after cooling to room temperature, and finally refluxed for 2 h. The reaction was then cooled to room temperature, poured into water and extracted with CH<sub>2</sub>Cl<sub>2</sub>. The organic layers were washed with water, dried over MgSO<sub>4</sub>, and concentrated in vacuo. The crude was purified by silica chromatography (eluent: ethyl acetate/ hexane = 1/10) to give <b>S4** as a yellow solid (11.52 g, 92%). M. p. 63–64 °C; IR (KBr) *v* 3097, 3073, 2924, 1637, 1565, 1459, 1412, 1384, 1330, 1154, 996, 809, 727 cm<sup>-1</sup>; <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 400 MHz)  $\delta$  7.62 (s, 1H), 7.45 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.36 (m, 2H), 7.12 (d, *J* = 4.8 Hz, 1H), 3.7 (s, 2H); <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, 100 MHz)  $\delta$  148.2, 147.6, 141.9, 137.8, 129.8, 128.3, 127.9, 122.8, 119.9, 118.3, 34.7; HRMS (*m*/*z*, FAB+ ) calcd. for C<sub>11</sub>H<sub>7</sub><sup>79</sup>BrS 249.9452, C<sub>11</sub>H<sub>7</sub><sup>81</sup>BrS 251.9431; found 249.9455, 251.9435.

**6-Bromo-4,4-dimethyl-4***H***-indeno[1,2-***b***]thiophene (1a). Methyl iodide (45 mmol, 2.8 mL) was added to a mixture of <b>S4** (5.02 g, 20 mmol) and potassium *tert*-butoxide (8 g, 71.3 mmol) in anhydrous THF (20 mL) at 0 °C. The iced bath was removed and the reaction mixture was stirred overnight at room temperature. The mixture was extracted with ethyl acetate and brine. The resulting organic phase was dried over MgSO<sub>4</sub>, concentrated in vacuo, and purified by silica chromatography (eluent: hexane)

to obtain **1a** as a colorless liquid (4.8 g, 86%). IR (KBr) *v* 3099, 3069, 2960, 2921, 2858, 1565, 1450, 1404, 1334, 1264, 1222, 1082, 989, 889, 815, 786 cm<sup>-1</sup>; <sup>1</sup>H NMR (Acetone- $d_6$ , 400 MHz)  $\delta$  7.65 (dd, J = 1.8, 0.6 Hz, 1H), 7.51 (d, J = 4.8 Hz, 1H), 7.43 (m, 2H), 7.17 (d, J = 5.2 Hz, 1H), 1.48 (s, 6H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$  158.4, 158.2, 138.7, 135.6, 130.0, 128.4, 126.0, 120.8, 120.2, 119.0, 46.0, 26.1; HRMS (m/z, FAB<sup>+</sup>) calcd. for C<sub>13</sub>H<sub>11</sub><sup>79</sup>BrS 277.9765, C<sub>13</sub>H<sub>11</sub><sup>81</sup>BrS 279.9744; found 277.9760, 279.9740.

4,4-Dimethyl-N,N-di-p-tolyl-4H-indeno[1,2-b]thiophen-6-amine (2a). To a 250 mL round flask was added di-p-tolylamine (3.26 g, 16.5 mmol), sodium tert-butoxide (4.3 g, 44.7 mmol), tributylphosphine (0.05 M toluene solution, 6 mL, 0.3 mmol), 1a (4.2 g, 15 mmol) and Pd(OAc)<sub>2</sub> (30 mg, 0.15 mmol) as the catalyst under Ar atmosphere. The mixture was injected with dry toluene (75 mL) and heated to reflux for 30 h. After cooling, the mixture was extracted with ethyl acetate and washed with an aqueous solution of NaCl and DI water. The combined organic layers were dried over MgSO<sub>4</sub> and evaporated to dryness. The crude product was further purified by silica chromatography (eluent: hexane) to obtain 2a as a pale yellow solid (5.71 g, 96%). M. p. 160–161 °C; IR (KBr) v 3022, 2957, 2920, 2856, 1605, 1576, 1508, 1469, 1419, 1340, 1318, 1274, 1237, 1074, 817 cm<sup>-1</sup>; <sup>1</sup>H NMR (Acetone-*d*<sub>6</sub>, 400 MHz) δ 7.37 (d, J = 4.8 Hz, 1H), 7.32 (d, J = 8.0 Hz, 1H), 7.15 (d, J = 2.0Hz, 1H), 7.10 (m, 5H), 6.95  $(dd, J = 6.6, 1.8Hz, 4H), 6.86 (dd, J = 8.2, 2.2 Hz, 1H), 2.29 (s, 6H), 1.38 (s, 6H); {}^{13}C$ NMR (CD<sub>2</sub>Cl<sub>2</sub>, 100 MHz) δ 158.1, 158.0, 146.4, 146.0, 139.8, 132.6, 131.2, 130.1, 126.8, 124.4, 122.5, 121.2, 119.5, 118.5, 26.4, 21.1; HRMS (*m/z*, FAB<sup>+</sup>) calcd. for C<sub>27</sub>H<sub>25</sub>NS 395.1708, found 395.1716.

*N*,*N*,4,4-tetra-*p*-tolyl-4*H*-indeno[1,2-*b*]thiophen-6-amine (2b). The synthetic procedure was similar to that of 2a. The crude product was further purified by silica chromatography (eluent: ethyl acetate/hexane = 1/20) to give 2b as a pale yellow solid (91%). M. p. 227–228 °C; IR (KBr) *v* 3024, 2917, 2858, 1604, 1577, 1508, 1472, 1312, 1276, 810, 761 cm<sup>-1</sup>; <sup>1</sup>H NMR (Acetone- $d_6$ , 400 MHz)  $\delta$  7.39 (m, 2H), 7.08 (m, 6H), 7.02 (m, 8H), 6.92 (m, 4H), 6.87 (dd, *J* = 8.2, 2.2 Hz, 1H), 2.28 (s, 6H), 2.26 (s, 6H); <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, 100 MHz)  $\delta$  154.9, 154.6, 146.2, 145.3, 131.9, 130.9, 136.3, 132.5, 131.1, 129.8, 129.0, 127.8, 127.0, 124.3, 123.1, 122.0, 121.4, 119.8, 63.3, 21.7, 21.6, 21.4; HRMS (*m*/*z*, FAB<sup>+</sup>) calcd. for C<sub>39</sub>H<sub>33</sub>NS 547.2334, found 547.2335.

2-(5-Bromopyrimidin-2-yl)-4,4-dimethyl-N,N-di-p-tolyl-4H-indeno-[1,2-b]-thioph en-6-amine (3a). n-BuLi (1.6 M, 5.9 mL, 9.4 mmol) was added dropwise to a solution of compound 2a (3.4 g, 8.6 mmol) in anhydrous THF (120 mL) cooled to -78 °C under Ar atmosphere. The reaction was stirred at this temperature for 0.5 h before the addition of tributyltin chloride (2.8 mL, 10 mmol) and the cooling bath was removed. The resulting mixture was kept stirring overnight, then quenched with H<sub>2</sub>O and extracted with diethyl ether. The combined organic phase was washed with H<sub>2</sub>O and brine, dried with anhydrous MgSO<sub>4</sub>, and evaporated under reduced pressure to obtain freshly prepared 4,4-dimethyl-N,N-di-p-tolyl-2-(tributylstannyl)-4H-indeno-[1,2-b]thiophen-6-amine, which was directly used in the following Stille reaction. A mixture of stannyl derivative (8.6 mmol), 5-bromo-2-iodopyrimidine (2.45 g, 8.6 mmol), and Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (302 mg, 0.43 mmol) in N<sub>2</sub> degassed DMF (100 mL) was heated at 80 °C under Ar atmosphere for 12 h. After cooling, the resulting mixture was extracted with diethyl ether, saturated potassium fluoride aqueous solution, ammonium chloride aqueous solution and brine. The organic phase was dried over MgSO<sub>4</sub> and the solvent was removed by rotary evaporation. The residue was purified by column chromatography on silica gel (eluent:  $CH_2Cl_2$ /hexane = 1/2) to afford **3a** as a light yellow solid (3.7 g, 78%). M. p. 287–288 °C; IR (KBr) v 3018, 2959, 2918, 2857, 1603, 1550, 1508, 1468, 1439, 1310, 1404, 1299, 1265, 1236, 1110, 814, 790 cm<sup>-1</sup>; <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 400 MHz)  $\delta$  8.67 (s, 2H), 7.91 (s, 1H), 7.31 (d, J = 8.4 Hz, 1H), 7.09 (m, 5H), 6.99 (m, 4H), 6.88 (dd, J = 8.2, 1.8 Hz, 1H), 2.32 (s, 6H), 1.42 (s, 6H); <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, 100 MHz) δ 160.4, 158.7, 158.4, 158.0, 147.7, 145.7, 145.6, 142.9, 133.1, 130.2, 130.0, 124.9, 123.9, 121.9, 120.5, 117.4, 116.3, 46.4, 26.4, 21.2; HRMS  $(m/z, FAB^+)$  calcd. for  $C_{31}H_{26}^{79}BrN_3S$  551.1031,  $C_{31}H_{26}^{81}BrN_3S$  553.1010; found 551.1027, 553.1025.

**2-(5-Bromopyrimidin-2-yl)***NNAA***-tetra***-p***-tolyl***-4H***-indeno**[1,2-*b*]**thiophen-6-am ine (3b).** The synthetic procedure was similar to that of **3a**. The residue was purified by column chromatography on silica gel (eluent: CH<sub>2</sub>Cl<sub>2</sub>/hexane = 1/3) to afford **3b** as a yellow solid (71%). M. p. 223–224 °C; IR (KBr) *v* 3022, 2918, 1859, 1602, 1509, 1447, 1412, 1320, 1295, 1271, 1175, 1111, 814, 751 cm<sup>-1</sup>; <sup>1</sup>H NMR (Acetone-*d*<sub>6</sub>, 400 MHz)  $\delta$  8.78 (s, 2H), 7.90 (s, 1H), 7.49 (d, *J* = 8.4 Hz, 1H), 7.09 (m, 14H), 6.95 (m, 3H), 6.90 (dd, *J* = 8.2, 2.2 Hz, 1H), 2.29 (s, 6H), 2.27 (s, 6H); <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, 100 MHz)  $\delta$  160.2, 158.0, 155.7, 155.6, 147.8, 146.7, 145.3, 143.4, 141.8, 136.9, 133.4, 130.2, 129.3, 128.0, 125.8, 125.1, 121.6, 121.0, 120.6, 116.5, 63.6, 21.3, 21.2; HRMS  $(m/z, FAB^+)$  calcd. for  $C_{43}H_{34}^{79}BrN_3S$  703.1657,  $C_{43}H_{34}^{81}BrN_3S$  705.1636; found 703.1656, 705.1621.

2-(6-(Di-p-tolylamino)-4,4-dimethyl-4H-indeno[1,2-b]thiophen-2-yl)pyrimidine-5 -carbaldehyde (4a). To a stirred solution of 3a (3.15 g, 5.7 mmol) in anhydrous THF (160 mL) at -100 °C was added dropwise a solution of n-BuLi (1.6 M, 3.7 mL, 5.9 mmol) under Ar atmosphere, and stirred for another 0.5 h. Anhydrous ethyl formate (4.6 mL, 57 mmol) was added dropwise to the reaction mixture and then stirred for 0.5 h at this temperature. The resulting mixture was quenched with 1.5 M HCl in THF solution (5 mL). The cooling bath was removed and the reaction mixture was stirred for overnight at room temperature. After addition of water, the mixture was extracted with ethyl acetate and the combined organic phase was washed with brine and dried over MgSO<sub>4</sub>. After removal of solvent under reduced pressure, the crude was purified by silica chromatography (eluent:  $CH_2Cl_2$ /hexane = 1/1) to yield 4a as a red solid (1.57 g, 55%). M. p. 251–252 °C; IR (KBr) v 3023, 2953, 2919, 2843, 1695, 1579, 1509, 1471, 1395, 1362, 1322, 1312, 1264, 1216, 1130, 816, 750 cm<sup>-1</sup>; <sup>1</sup>H NMR  $(CD_2Cl_2, 400 \text{ MHz}) \delta 9.99 \text{ (s, 1H)}, 9.01 \text{ (s, 2H)}, 8.08 \text{ (s, 1H)}, 7.35 \text{ (d, } J = 8.4 \text{ Hz}, 1\text{H}),$ 7.10 (m, 5H), 7.01 (m, 4H), 6.89 (dd, J = 8.2, 2.2 Hz, 1H), 2.33 (s, 6H), 1.44 (s, 6H); <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, 100 MHz) δ 188.6, 165.1, 159.0, 158.8, 148.8, 148.4, 145.4, 143.0, 133.4, 130.3, 129.4, 126.1, 125.7, 125.2, 121.5, 121.0, 116.9, 46.4, 26.4, 21.2; HRMS  $(m/z, FAB^+)$  calcd. for C<sub>32</sub>H<sub>27</sub>N<sub>3</sub>OS 501.1875, found 501.1882.

**2-(6-(Di***p*-tolylamino)-4,4-di-*p*-tolyl-4*H*-indeno[1,2-*b*]thiophen-2-yl)pyrimidine-5 -carbaldehyde (4b). The synthetic procedure was similar to that of 4a. The crude was purified by silica chromatography (gradient eluent: CH<sub>2</sub>Cl<sub>2</sub>/hexane = 1/1 to 2/1) to yield 4b as a red solid (80%). M. p. 260–261 °C; IR (KBr) *v* 3024, 2918, 2833, 1698, 1578, 1509, 1447, 1409, 1321, 1295, 1276, 1216, 814, 751 cm<sup>-1</sup>; <sup>1</sup>H NMR (Acetone-*d*<sub>6</sub>, 400 MHz)  $\delta$  10.10 (s, 1H), 9.10 (s, 2H), 8.05 (s, 1H), 7.54 (d, *J* = 8.4 Hz, 1H), 7.09 (m, 14H), 6.96 (m, 3H), 6.91 (dd, *J* = 8.2, 2.2 Hz, 1H), 2.30 (s, 6H), 2.28 (s, 6H); <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, 100 MHz)  $\delta$  188.6, 164.9, 158.9, 156.1, 156.0, 149.7, 148.4, 145.1, 143.4, 141.7, 137.0, 133.7, 130.3, 129.7, 129.4, 128.0, 125.9, 125.3, 121.4, 121.3, 120.1, 63.6, 21.3, 21.2; HRMS (*m*/*z*, FAB<sup>+</sup>) calcd. for C<sub>44</sub>H<sub>35</sub>N<sub>3</sub>OS 653.2501, found 653.2497.

2-((2-(6-(Di-*p*-tolylamino)-4,4-dimethyl-4*H*-indeno[1,2-b]thiophen-2-yl-pyrimidin -5-yl)methylene)malononitrile (MIDTP). A mixture of aldehyde derivative 4a (1.02

g, 2 mmol), malononitrile (264 mg, 4 mmol) and neutral Al<sub>2</sub>O<sub>3</sub> (1 g) in toluene (30 mL) was heated at 80 °C for 1 h under N<sub>2</sub> atomosphere. After cooling to room temperature, the reaction mixture was diluted with toluene and the Al<sub>2</sub>O<sub>3</sub> residue was removed by filtration and washed several times with CHCl<sub>3</sub>. The resulting filtrate was evaporated to dryness and purified by silica chromatography (eluent: CH<sub>2</sub>Cl<sub>2</sub>/hexane = 1/1). The solid was reprecipitated three times with hexane/CH<sub>2</sub>Cl<sub>2</sub> and filtered to ensure the purity for device fabrication. MIDTP (920 mg, 84%) was obtained as a black solid after dried under vacuum for 12 h. M. p. 301 °C (DSC); IR (KBr) v 3020, 2955, 2923, 2865, 2225, 1574, 1506, 1444, 1381, 1375, 1320, 1296, 1247, 1221, 1128, 821, 763 cm<sup>-1</sup>; <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 400 MHz) δ 9.08 (s, 2H), 8.08 (s, 1H), 7.64 (s, 1H), 7.36 (d, J = 8.4 Hz, 1H), 7.10 (m, 5H), 7.01 (m, 4H), 6.88 (dd, J = 8.6, 2.2 Hz, 1H), 2.33 (s, 6H), 1.43 (s, 6H); <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, 100 MHz) δ 164.3, 159.4, 159.1, 158.8, 153.6, 150.5, 148.9, 145.3, 142.7, 133.7, 130.4, 129.0, 126.9, 125.4, 121.9, 121.4, 121.3, 116.4, 114.0, 133.2, 82.7, 46.4, 26.4, 21.2; HRMS (*m/z*, FAB<sup>+</sup>) calcd. for C<sub>35</sub>H<sub>27</sub>N<sub>5</sub>S 549.1987, found 549.1981; Anal. calcd. for C<sub>35</sub>H<sub>27</sub>N<sub>5</sub>S: C 76.48; H 4.95; N 12.74; S 5.83, found C 76.06; H 5.02; N 12.64; S 5.95.

**2-((2-(6-(Di***p***-tolylamino)-4,4-di***p***-tolyl-4***H***-indeno-[1,2-***b***]-thiophen-2-yl)pyrimid in-5-yl)methylene)malononitrile (TIDTP). The synthetic procedure was similar to that of MIDTP. The crude was purified twice by silica chromatography (eluent: CH\_2Cl\_2/hexane = 1.5/1). The solid was reprecipitated twice with pentane/ CH\_2Cl\_2 and filtered to ensure the purity for device fabrication. TIDTP (66%) was obtained as a black solid after dried under vacuum for 12 h. M. p. 248 °C (DSC); IR (KBr)** *v* **3024, 2918, 1861, 2226, 1575, 1508, 1447, 1393, 1392, 1321, 1264, 1240, 816, 751 cm<sup>-1</sup>; <sup>1</sup>H NMR (Acetone-***d***<sub>6</sub>, 400 MHz) \delta 9.23 (s, 2H), 8.31 (s, 1H), 8.08 (s, 1H), 7.56 (d,** *J* **= 8.0 Hz, 1H), 7.11 (m, 14H), 6.97 (m, 3H), 6.91 (dd,** *J* **= 8.4, 2.4 Hz, 1H), 2.30 (s, 6H), 2.28 (s, 6H); <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, 100 MHz) \delta 164.1, 158.7, 156.4, 156.2, 153.5, 151.3, 148.8, 145.0, 143.1, 141.5, 137.1, 133.9, 130.3, 129.4, 129.3, 128.7, 128.0, 127.3, 125.4, 122.0, 121.8, 121.2, 119.8, 113.9, 113.1, 83.1, 63.5, 21.3, 21.2; HRMS (***m/z***, FAB<sup>+</sup>) calcd. for C<sub>47</sub>H<sub>35</sub>N<sub>5</sub>S 701.2613, found 701.2607; Anal. calcd. for C<sub>47</sub>H<sub>35</sub>N<sub>5</sub>S: C 80.43; H 5.03; N 9.98; S 4.57, found C 80.24; H 4.96; N 10.01; S 4.76.** 

### **Theoretical Modeling**

All the molecular conformations and photopysical properties of molecules were performed based on the density functional theory (DFT) at the CAM-B3LYP (Coulomb-attenuating method-B3LYP) level with the 6-31G(d,p) basis set using the Gaussian 09 program package. The S<sub>0</sub> and S<sub>1</sub> geometries of all molecules were fully optimized without symmetric constraints with solvent effects included by the polarizable continuum model (PCM) using the dielectric constant of dichloromethane. The time-dependent DFT (TDDFT) calculation shows the vertical lowest singlet excitation wavelengths, oscillator strengths and molecular orbital compositions in terms of corresponding contributions. The EPMs presented in this paper were performed at M06-2X/6-31+G(d,p)<sup>121</sup> level. Note that electrostatic potential was mapped onto the total electron density isosurface of 0.05, with red surface areas indicating high electron density (negative charge) and blue for areas enclosing low electron density (positive charge).



**Figure S1.** Isodensity surface plots of the lowest-energy transitions for **MIDTP** (A) and **TIDTP** (B), where blue denoted HOMOs and pink symbolized LUMOs.

**Table S1.** Computed lowest-energy excitation maxima wavelengths ( $\lambda_{calc}$ ), energy levels ( $E_{HOMO}$ ), oscillator strengths (f), and MO compositions in terms of corresponding contributions at TDDFT//CAM-B3LYP/6-31G(d,p) level.

Molecules	$\lambda_{calc} [nm]$	$E_{\rm HOMO}[\rm eV]$	f	MO Composition
MIDTP	601	-5.98	2.32	$83\% \text{ HOMO} \rightarrow \text{LUMO}$
DIDTP	597	-6.02	1.85	83% HOMO $\rightarrow$ LUMO



**Figure S2.**  $\mu_{tr}$  of a) **MIDTP** and b) **TIDTP** for the lowest-energy excitations computed from TDDFT//CAM-B3LYP/6- 31G(d,p) modeling. Face-on and side-on views included  $\mu_{tr}$  depicted by arrows with the x-axis aligned along the long molecular axis.

# **Thermal Analyses**

Thermogravimetric analysis (TGA) was taken with a TA instrument 5100 thermal analysis system. The thermal stability of the samples under a nitrogen atmosphere was determined by measuring their 5% weight loss while heating proceeded at a rate of 10 °C/min from room temperature to 800 °C. The differential scanning calorimetry (DSC) analyses were performed on a TA Instruments DSC Q-20 with a heating rate of 5 °C/min under nitrogen. The 2<sup>nd</sup> heating and cooling scan cycles were applied to determine the thermal transition temperatures.



Figure S3. TGA traces of MIDTP and TIDTP with a heating rate of 10 °C min<sup>-1</sup> under  $N_2$  atmosphere.



Figure S4. DSC thermograms of MIDTP and TIDTP with a heating/cooling rate of 5  $^{\circ}$ C min<sup>-1</sup> under N<sub>2</sub> atmosphere.

# **Single-Crystal Structure Determinations**

Single crystal X-ray crystallographic measurement was probed on Agilent Xcalibur (Atlas, Gemini ultra) diffractometer using graphite-monochromatic radiation (Cu-K $\alpha$ , 1.54178 Å) at 150 (2) K and 200 (2) K for **TIDTP** and **MIDTP**, respectively. Data and  $\omega$ -scans were collected with CrysAlis Pro (Agilent) software for all observed reflections. Cell refinement and data reduction were performed with CrysAlis Pro (Agilent) software. SHELXS97 (Sheldrick, 2008) was applied for solving structures by direct methods, and refining structures by full-matrix least-squares techniques on F<sup>2</sup>. The crystallographic data for **TIDTP** (CCDC: 1045235) and **MIDTP** (CCDC: 1045236) can be obtained from the Cambridge Crystallographic Data Centre.



**Figure S5**. Single crystal X-ray structure analysis for **MIDTP**: views of individual molecule as seen perpendicular to (top) and along (bottom) the plane of conjugated backbone.



**Figure S6.** Illustration of **MIDTP** in layered packing. (a) Side-on view down the long molecular axes and the pitch angle. N-substituted tolyl groups and hydrogen atoms were omitted for clarity. (b) Side-on view down the short molecular axes and the roll angle. (c) Side-on view of slip-staircase sheets.



**Figure S7**. Perspective views of **TIDTP**: as seen along the (1 -3 3) plane with long (left) and short (right) molecular axes depicted. All tolyl-subunits and hydrogen atoms were omitted for clarity.



**Figure S8.** EPMs of antiparallel dimers. (a) Coplanar centrosymmetric dimer with a C-H···S distance of 5 Å (left), and a C-H···S van der Waals distance of 2.92 Å for the experimentally observed value in **MIDTP** crystal lattice (right). (b) Cofacial  $\pi$ -stacked dimeric unit with a  $\pi$ -scaffold distance in dimer of 6.3 Å (left), and 3.4 Å for the value derived from **TIDTP** single-crystal structure (right). Color mapping of EPMs are schemed to represent the spreading of electrons, typically, with color surface shaded in red containing electron-rich moieties (net negative charge), blue for

electron-poor areas (net positive charge) and green for spaces enclosing balanced positive and negative charges (overall neutral charge).

# **Fabrication and Characterization of OFET Devices**

A heavily *n*-doped Si wafer with a SiO<sub>2</sub> layer of 300 nm (capacitance of 11  $nF/cm^2$ ) was used as the substrate with Si wafer serving as the gate electrode and SiO<sub>2</sub> as the dielectric. In the PAC method, crystal arrays of MIDTP and TIDTP were prepared on glass and PTS-treated SiO<sub>2</sub>/Si substrates from their chlorobenzene (CB), o-dichlorobenzene (ODCB) and dichloromethane (DCM) solutions at ambient condition. The process time was between 40 sec (DCM) to around 30 minutes (ODCB) depending on the boiling points of the solvents. Gold source and drain electrodes (40 nm in thickness) were deposited by vacuum evaporation on the MIDTP crystal arrays and TIDTP amorphous thin film on ODTS-treated SiO<sub>2</sub>/Si substrates through a shadow mask (channel dimension:  $W/L = 1500 \ \mu m/25 \ \mu m$ ), affording a bottom-gate, top-contact device configuration. Characterization of OFET devices was carried out using an Agilent 4156C Semiconductor Parameter Analyzer under an atmosphere of N<sub>2</sub> at room temperature. The field-effect mobility was determined in the saturation regime using the equation,  $I_{\rm DS} = (\mu W C_i/2L) (V_{\rm G} - V_{\rm th})^2$ , where  $I_{\rm DS}$  is the source-drain current,  $\mu$  is the field-effect mobility, W is the channel width, L is the channel length,  $C_{\rm i}$  is the capacitance per unit area of the gate dielectric layer,  $V_{\rm G}$  is the gate voltage, and  $V_{\text{th}}$  is the threshold voltage.



**Figure S9**. The OM images for **MIDTP** crystal arrays prepared on glass substrates with different solvents: a) CB, b) ODCB, and c) DCM.



**Figure S10**. The morphology of **TIDTP** on given substrates by PDMS-assisted crystallization (PAC) processed with DCM solvent: a) OM image of **TIDTP** on glass substrate; b) POM image of **TIDTP** on glass substrate; c) OM image of the **TIDTP** OFET using ODTS-SiO<sub>2</sub>/Si substrate.



**Figure S11**. a) Output curves and b) transfer characteristics of OFETs employed **TIDTP** thin films processed by the PAC method.

#### **Characterization of Crystalline Microwires by Electron Microscopy**

**MDITP** crystal arrays were prepared on carbon-coated mica substrates by the PAC method. The crystal arrays on the carbon film was floated onto a water surface and picked up by copper grids. The samples were dried under vacuum overnight before the transmission electron microscopy (TEM) observation. TEM images were performed in bright-field and high-resolution mode by a JEOL JEM-2010 transmission electron microscope operated at accelerating voltage of 200 kV and selected area electron diffraction (SAED) was also obtained at accelerating voltage of 200 kV. For crystal structure modeling, Material studio 6.0 software from Accelrys was used to build up the lattice models of **MIDTP**. The lattice models were built according to the single crystal structures of **MIDTP**.

#### **Grazing Incident X-ray Diffraction Measurement**

The grazing incident X-ray diffraction (GIXRD) for pristine thin-film diffractions were collected at ambient condition on a Rigaku SmartLab high-resolution X-ray diffractometer with a Cu (1.54178 Å) source at the Materials Research Laboratory (MRL) X-ray Facility, University of California, Santa Barbara. Thin films of materials were prepared by vacuumed deposition on top of ITO/MoO<sub>3</sub> substrates. The angle of incident beam to thin films was aligned to 0.18° for penetrating fully the active layer and reducing the background signals from substrates. Out-of-plane GIXRD profiles were obtained along with out-of-plane direction (perpendicular to the substrate of film surface; defined as the z direction). These profiles were expressed as a function of scattering vector of  $q_z$  (out-of-plane).



**Figure S12.** XRD results for **MIDTP**. a) The simulated powder profile (bottom) from single-crystal analysis and out-of-plane GIXRD patterns of the as-deposited (middle) and annealed (top) film. Visual perspectives of relative alignment for b)  $(1 \ 3 \ -2)$  and  $(1 \ 2 \ 0)$ , and c)  $(0 \ 1 \ -1)$  and  $(1 \ 2 \ 0)$  lattice planes, which corresponded to crystalline peaks assignable in GIXRD. All tolyl-subunits and hydrogen atoms were omitted in (b,c) for clarity.



**Figure S13.** XRD results for **TIDTP**. a) The simulated powder profile (bottom) from single-crystal analysis and out-of- plane GIXRD patterns of the as-deposited (middle) and annealed (top) film. b) An illustration of the (1 -1 1) lattice plane correlated to the crystalline feature obtained from the annealed film. All tolyl-subunits and hydrogen atoms in (b) were omitted for clarity.

# Atomic force microscopy (AFM)

AFM images were taken using a Bruker Dimension Icon atomic force microscopy. The film preparation conditions for the AFM measurements were kept the same as device fabrication for the accurate comparisons.



**Figure S14**. AFM topographic images of pristine films: a) as-deposited **TIDTP** film; b) annealed **TIDTP** film; (C) as-deposited **MIDTP** film; (D) annealed **MIDTP** film.

#### **Mobility Measurement**

The hole-only diodes were fabricated by sandwiching the evaporated pristine-films (100 nm) between the 1-nm-thick MoO<sub>3</sub> deposited-ITO and the MoO<sub>3</sub> (10 nm)/Al (150 nm) top contact that gave a deep work function. For the annealed diodes, the pristine films were annealed for 20 min at 135 °C before the deposition of top contact. The current density-voltage (*J-V*) characteristics of devices were measured with a Keithley 2636A SourceMeter and fitted to the space-charge limited current (SCLC) Mott-Gurney equation  $J = \frac{9}{8} \varepsilon \varepsilon_0 \mu_0 \frac{V^2}{L^3} \exp\left(\frac{0.89\beta}{\sqrt{L}}\sqrt{V}\right)$ , where *J* is the current density, *V* is the bias voltage, *L* is the thickness of the active layer,  $\mu_0$  is the field-activation factor and  $\varepsilon$  is the dielectric constant, which was assumed to be 3 as a typical value for organic materials.



**Figure S15**. Hole mobilities for the as-deposited and annealed **TIDTP** and **MIDTP** neat films.

Table S2. Performances parameters	of TIDTP	and <b>MIDTP</b>	SCLC Devices.
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Devices	$\beta  [cm^{0.5}  V^{0.5} ]$	Zero field mobility [cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> ]
TIDTP w/o anneal	2.5E-3	2.11E-6
TIDTP w/ anneal	3.16E-3	4.31E-6
MIDTP w/o anneal MIDTP w/ anneal	5.28E-3 1.04E-3	4.74E-7 3.59E-4

#### Solar Cell Fabrication and Testing

Organic materials such as commercially available 4,7-diphenyl-1,10phenanthroline (Bphen), 1, 3, 5-tri[(3-pyridyl)-phen-3-yl]benzene (TmPyPB), C<sub>60</sub> and C<sub>70</sub> were purified by thermal-gradient vacuumed sublimation. All devices were prepared with a transparent ITO as anode with sheet resistance ~15  $\Omega$ /sq. ITO substrates were cleaned in ultrasonic bath with deionized water, acetone and methanol for 15 min, and then treated by ultraviolet-ozone for 30 min before being loaded into a high vacuum chamber (base pressure  $\sim 1 \times 10^{-6}$  torr). Organic layers were thermally evaporated at the rate of 0.1-0.2 nm/s and Ag was deposited at the rate of 0.4 nm/s through a shadow mask to define a cell area of  $\sim 5 \text{ mm}^2$ . The deposition was performed with the substrate held at room temperature. Thicknesses were monitored using a crystal oscillator during deposition and were verified later with spectroscopic ellipsometry. The accurate device areas were measured device-by-device using calibrated optical microscope. Finally the fabricated cells were encapsulated using a UV-cured sealant (Epowide EX, Everwide Chemical Co.) in a N2 glove box. The current density versus voltage (J-V) characteristics were measured with a Keithley Model 2636A SourceMeter in the dark and under AM 1.5G simulated solar illumination with an intensity of 100 mW/  $cm^2$  (1 sun, calibrated by NREL-traceable KG5 filtered Silicon reference cell). The external quantum efficiency (EQE) spectra were taken by illuminating a chopped monochromatic light with a continuous-wave bias white light (from halogen lamp) on the solar cells. The photocurrent signals were then extracted with lock-in technique using a current Stanford Research System preamplifier followed by a lock-in AMETEK amplifier. The EQE measurement was fully computer-controlled, and the intensity of the monochromatic light was calibrated with an NIST-traceable optical power meter (Ophir Optronics). Organic films for photoelectron spectroscopy and ellipsometry measurements were vacuum deposited on fused silica substrates. The HOMO values of thin films were obtained with a Riken Keiki Co. Ltd. photoelectron spectrometer. Ellipsometry measurements were carried out with J. A. Woollam Inc. V-VASE variable-angle spectroscopic ellipsometer.



**Figure S16.** PMHJ photovoltaic characteristics with device structure: ITO/MoO<sub>3</sub>/Donor/Donor:C<sub>70</sub> (1:1)/C<sub>70</sub>/TmPyPB/Ag for **TIDTP** (a,b) and **MIDTP** (c,d) optimized by different thickness of active layers. All devices were recorded under AM 1.5G solar illumination (100 mw cm<sup>-2</sup>).

**Table S3.** Photovoltaic parameters of PMHJ solar cells(ITO/MoO<sub>3</sub>/Donor/Donor:C70 (1:1)/C70/TmPyPB/Ag) adpoted MIDTP and TIDTPwith different thickness of active layers.

Device	$J_{\rm sc} [{ m mA~cm}^{-2}]$	$V_{\rm oc}[{ m V}]$	FF	PCE [%]
<b>TIDTP</b> :C <sub>70</sub> (35 nm)	8.71	0.83	0.40	2.92
<b>TIDTP</b> :C <sub>70</sub> (40 nm)	9.78	0.85	0.41	3.41
<b>TIDTP</b> :C <sub>70</sub> (45 nm)	9.33	0.86	0.41	3.31
<b>TIDTP</b> :C <sub>70</sub> (50 nm)	9.43	0.85	0.39	3.08
<b>MIDTP</b> :C <sub>70</sub> (20 nm)	8.95	0.83	0.45	3.37
<b>MIDTP</b> :C <sub>70</sub> (30 nm)	10.72	0.82	0.47	4.12
<b>MIDTP</b> :C <sub>70</sub> (35 nm)	11.12	0.82	0.46	4.22
<b>MIDTP</b> :C <sub>70</sub> (40 nm)	10.53	0.78	0.40	3.25
<b>MIDTP</b> :C <sub>70</sub> (45 nm)	10.98	0.80	0.40	3.52

<b>MIDTP</b> :C <sub>70</sub> (50 nm)	10.95	0.80	0.38	3.3
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Grazing-incidence wide-angle X-ray scattering (GIWAXS) for all blended thin films was performed with the angle of incident beam aligned precisely to  $0.2^{\circ}$  at beam-line 23A of National Synchrotron Radiation Research Center (NSRRC) in Taiwan. The photon energy of beam was 10 keV and a two-dimensional (2D) detector was used to collected 2D GIWAXS patterns. One-dimensional (1D) GIWAXS profiles are reduced from the 2D GIWAXS patterns, including in-plane and out-of-plane GIWAXS profiles. In-plane and out-of-plane GIWAXS profiles were derived along with in-plane direction (parallel to the substrate or film surface; defined as the xy direction,  $q_{xy}$ ) and out-of-plane direction ( $q_z$ ), respectively.



Figure S17. a) Out-of-plane and b) in-plane GIWAXS profiles.

### References

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