

*Electronic Supplementary Information*

**Hydrogen-bonded oligothiophene rosettes with benzodithiophene terminal unit:  
self-assembly and application to bulk heterojunction solar cells**

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## Materials and methods

Column chromatography was performed using 63–210  $\mu\text{m}$  silica gel. All other commercially available reagents and solvents were of reagent grade and used without further purification. The solvents for the preparation of the assemblies were all spectral grade and used without further purification.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on Bruker DPS300 and JEOL JNM-ECA500 NMR spectrometers and chemical shifts are reported in ppm ( $\delta$ ) with the signal of TMS as internal standard. APCI-MS spectra were measured on an Exactive (Thermo Fisher). FT/IR spectra were recorded on JASCO FT/IR-4100 spectrometer. UV-vis spectra were recorded on a JASCO V660 spectrophotometer. The HOMO levels were measured by photoelectron yield spectroscopy (MODEL AC-3, RIKEN KEIKI. Co.,Ltd) under atmospheric pressure. AFM images were acquired under ambient conditions using Multimode 8 Nanoscope V (Bruker AXS) in Peak Force Tapping (Scanasyt) mode. Silicon cantilevers (SCANASYST-AIR) with a spring constant of 0.4 N/m and frequency of 70 kHz (Bruker AXS) were used. Synchrotron radiation X-ray diffraction measurements were performed at BL45XU in SPring-8 with the approval of the RIKEN SPring-8 Center (Proposal Nos. 20140056 and 20150068). Molecular mechanics calculations were performed on MacroModel version 10.4 using AMBER\* force field.

## Scanning tunneling microscopy (STM)

Solutions of compound in 1-phenyloctane (98%, Aldrich) were prepared. A droplet of these solutions was then deposited on a graphite substrate. STM imaging of the samples was performed at the liquid–solid interface using a Pico-SPM (Molecular Imaging, Agilent Technology) scanning tunneling microscope. Cut Pt/Ir tips were used to obtain constant current images at room temperature with a bias voltage applied to the sample. STM images were processed and analyzed using the application FabViewer.<sup>1</sup>

## Fabrication of organic solar cells

Bulk heterojunction solar cell devices were fabricated on indium-tin oxide (ITO) coated glass. The ITO glass substrates were subsequently cleaned with acetone and 2-propanol in ultrasonic bath. The resultant ITO substrates were then exposed to UV-ozone for 5 mins and coated with PEDOT:PSS [poly(3,4-ethylene dioxythiophene):poly(styrene sulfonate)](AI 4083, thickness: ca. 30 nm). The substrates were heated for 20 min at 120 °C to remove residual water. In a  $\text{N}_2$  glove box, 0.5 mL of chloroform solutions containing  $\text{PC}_{61}\text{BM}$  (Luminescence Technology Corp., Taiwan Province) and oligothiophene derivatives were spin-coated (1000 rpm for 30 sec) onto the substrate. The thickness of the resulting BHJ films was determined by using a DEKTAK surface profiler (Bruker AXS). The substrates were then moved to high-vacuum chamber, and the top electrode was evaporated through a shadow mask (Ca:10 nm, Al:90 nm) to give solar cells with an active area of 0.04  $\text{cm}^2$ . Finally, the

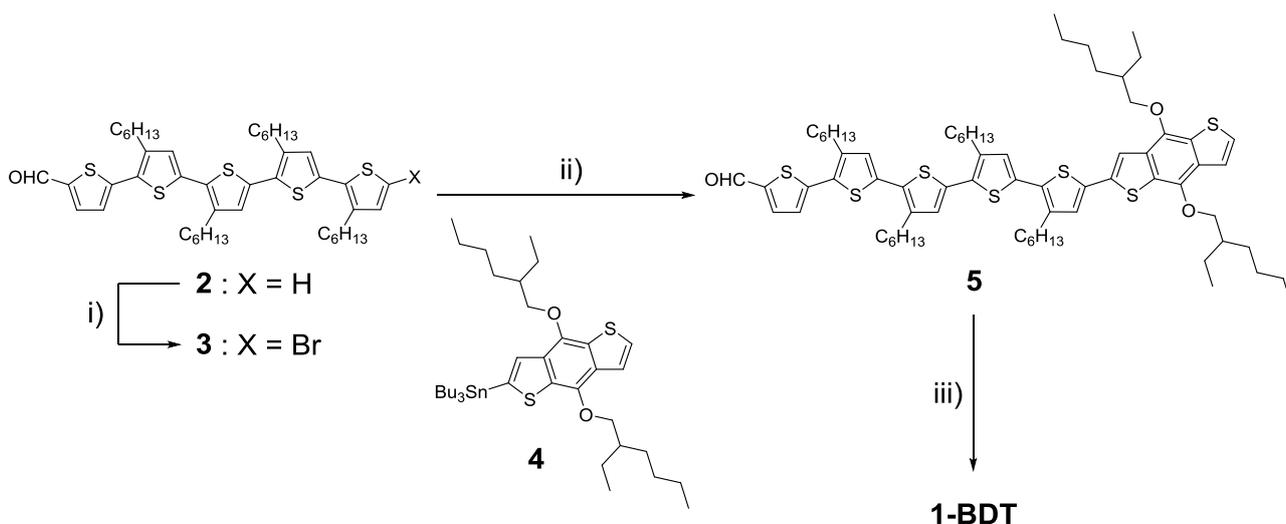
devices were encapsulated by a glass lid in the nitrogen glove box system. The *J-V* characteristics of the solar cells were evaluated by using a Keithley 2400 source-measure unit. The AM 1.5 G light was provided by a filtered Xe lamp. The intensity of  $100 \text{ mW cm}^{-2}$  of the AM 1.5 G light was determined by using a calibrated inorganic solar cell from the National Institute of Advanced Industrial Science and Technology (Japan). No spectral mismatch factor was in the calculation of the efficiency.

## Fabrication of organic field-effect transistor

OFET devices were fabricated on  $\text{SiO}_2/\text{Si}$  substrates ( $\text{SiO}_2/\text{Si}$ , thickness: ca. 300 nm). The  $\text{SiO}_2$  substrates were subsequently cleaned with acetone and 2-propanol in ultrasonic bath. Thin films of oligothiophene derivatives were prepared by spin-coating (1500 rpm)  $\text{CHCl}_3$  solutions. After drying the solvent, the substrates were annealed at a temperature for 10 min to give active layers with thicknesses ranging from 100 to 120 nm. Subsequently, top-contact gold electrodes (Au, thickness: ca. 70 nm) were deposited through shadow masks under vacuum to define channels width and length of 5.5 mm and 50  $\mu\text{m}$ , respectively. The OFET device measurements were performed using a semiconductor parameter analyzer (Agilent 4155C) at room temperature in a nitrogen glove box where the concentration of  $\text{H}_2\text{O}$  and  $\text{O}_2$  was less than 1 ppm. The hole mobilities of oligothiophene derivatives were calculated in the saturation regime of transfer characteristics.

## Synthesis and analytical data

**1-BDT** was synthesized according to Scheme S1. The synthesis of compounds **2** and **4** were reported previously.<sup>2,3</sup>



**Scheme S1.** Synthesis of **1-BDT**. i) NBS,  $\text{CHCl}_3/\text{acetic acid}$ ,  $0\text{ }^\circ\text{C} \rightarrow \text{r.t.}$ , 4.0 h; ii)  $[\text{Pd}(\text{PPh}_3)_4]$ , DMF, microwave,  $150\text{ }^\circ\text{C}$ , 30 min; iii) barbituric acid, EtOH, reflux, 2.5 h.

### Compound 3

#### 5'''-bromo-3',3'',3''',3''''-tetrahexyl-[2,2':5',2'':5'',2''':5''',2''''-quinquethiophene]-5-carbaldehyde:

To an ice-cooled 2:1 CHCl<sub>3</sub>/acetic acid mixture (15 mL) containing **2** (102 mg, 0.131 mmol), *N*-bromosuccinimide (23.5 mg, 0.132 mmol) was added in two portions with at interval of 10 min. The reaction mixture was warmed to r.t. and stirred for 4 h. The resulting mixture was diluted with CHCl<sub>3</sub>, and washed twice with sat. aq. NaHCO<sub>3</sub>. The organic layer was dried with Na<sub>2</sub>SO<sub>4</sub>, filtered and evaporated to dryness to give compound **3** as red liquid (111 mg, 99%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 293 K):  $\delta$  = 9.89 (s, 1H), 7.72 (d, *J* = 4.0 Hz, 1H), 7.24 (d, *J* = 4.0 Hz, 1H), 7.01 (s, 1H), 6.96 (s, 2H), 6.89 (s, 1H), 6.88 (s, 1H), 2.85–2.69 (m, 8H), 1.75–1.56 (m, 8H), 1.42–1.25 (m, 24H), 0.92–0.86 (m, 12H).

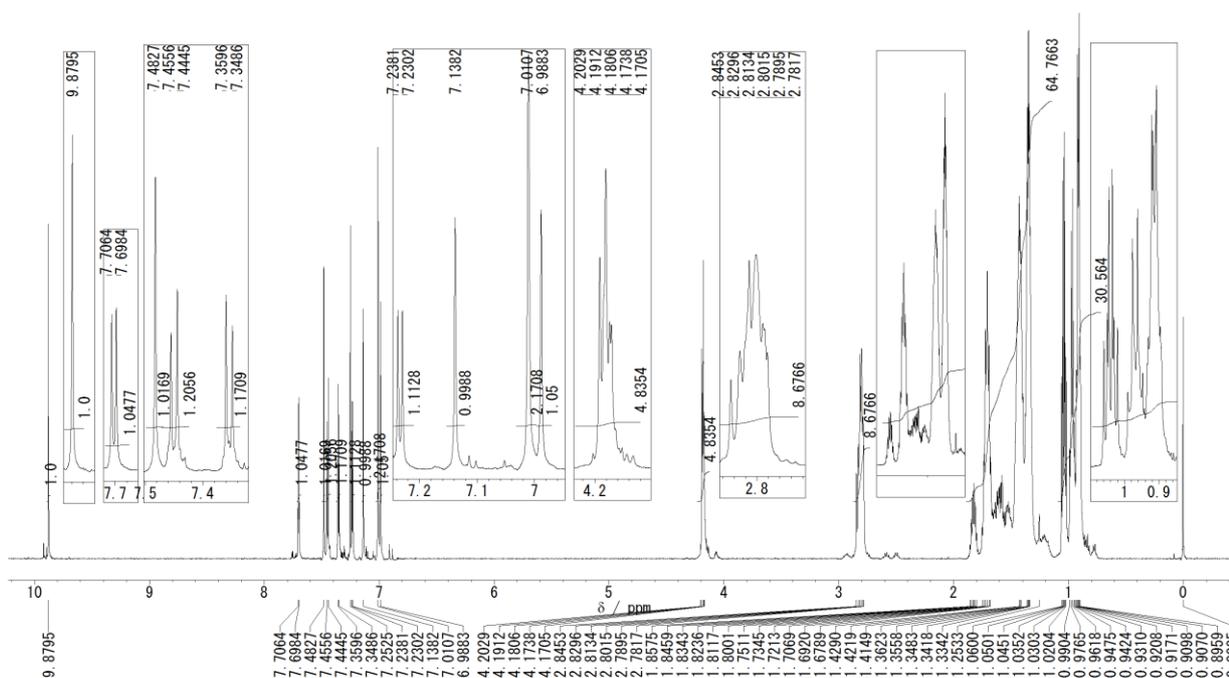
### Compound 5

#### (5'''-(4,8-bis((2-ethylhexyl)oxy)benzo[1,2-*b*:4,5-*b'*])dithiophen-2-yl)-3',3'',3''',3''''-tetrahexyl-[2,2':5',2'':5'',2''':5''',2''''-quinquethiophene]-5-carbaldehyde):

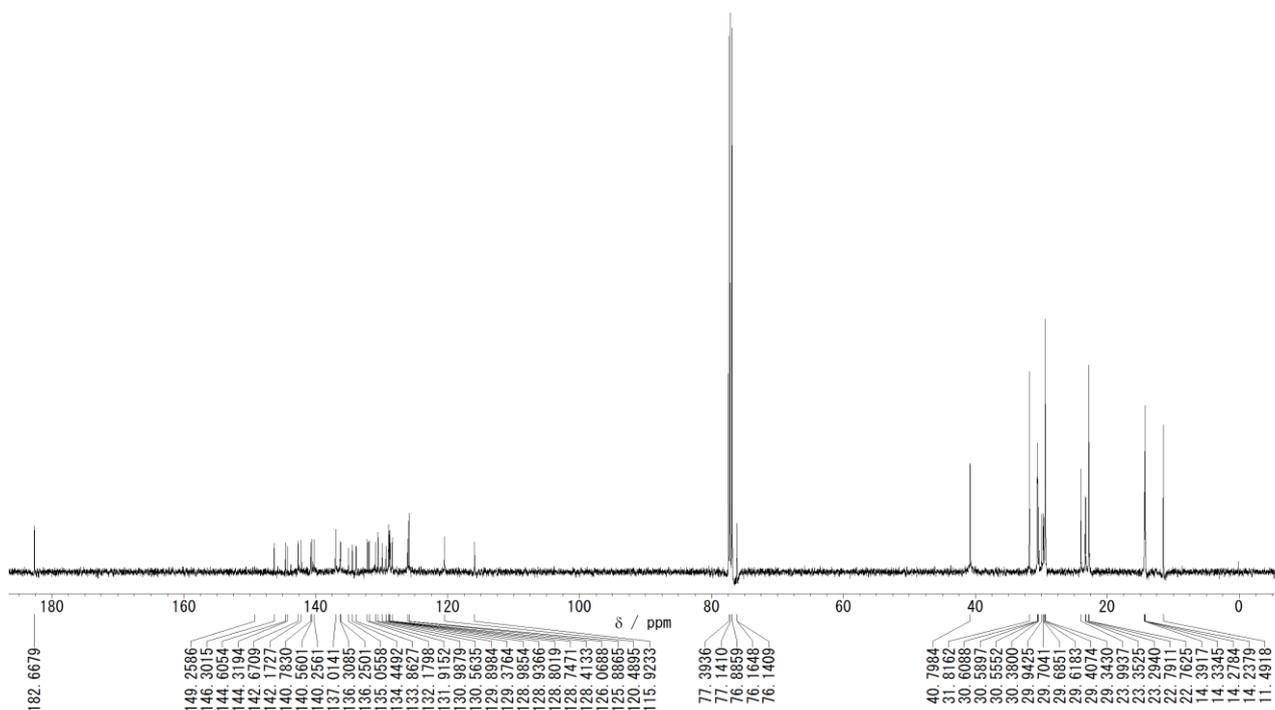
A 10-mL of microwave reactor vessel was charged with **3** (369 mg, 0.431 mmol), **4** (624 mg, 0.848 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (28.2 mg, 0.0244 mmol) and DMF (4 mL), and the vessel was placed into a microwave reactor. The reaction temperature and period was set to 150 °C and 30 min, respectively. After completion of the reaction, the mixture was diluted with ethyl acetate and washed twice with water and once with brine. The organic layer was dried with Na<sub>2</sub>SO<sub>4</sub>, filtered and evaporated to dryness. The resulting liquid was purified by column chromatography (10 w/w% K<sub>2</sub>CO<sub>3</sub>-silica gel, eluent: CHCl<sub>3</sub>/hexane = 1:1 (v/v)) to give pure compound **5** as orange liquid (339 mg, 64%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 293 K):  $\delta$  = 9.88 (s, 1H), 7.70 (d, *J* = 4.0 Hz, 1H), 7.48 (s, 1H), 7.45 (d, *J* = 5.5 Hz, 1H), 7.35 (d, *J* = 5.5 Hz, 1H), 7.23 (d, *J* = 4.0 Hz, 1H), 7.14 (s, 1H), 7.01 (s, 2H), 6.99 (s, 1H), 4.20–4.17 (m, 4H), 2.85–2.78 (m, 8H), 1.86–1.25 (m, 50H), 1.06–0.90 (m, 24H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, 293 K):  $\delta$  = 182.67, 146.30, 144.61, 144.32, 142.67, 142.17, 140.78, 140.56, 140.26, 137.01, 136.31, 136.25, 135.06, 134.45, 133.86, 132.18, 131.92, 130.99, 130.56, 129.90, 129.38, 128.99, 128.94, 128.80, 128.75, 128.41, 126.07, 125.89, 120.49, 115.92, 76.16, 76.14, 40.80, 31.82, 30.61, 30.59, 30.56, 30.38, 29.94, 29.70, 29.69, 29.62, 29.41, 29.34, 23.99, 23.35, 23.29, 22.79, 22.76, 14.39, 14.33, 14.28, 14.24, 11.49; HRMS (APCI): *m/z* calcd. for C<sub>71</sub>H<sub>97</sub>O<sub>3</sub>S<sub>7</sub> 1221.5477 [M+H]<sup>+</sup>, found 1221.5487.

**1-BDT:** A mixture of **5** (116 mg, 0.095 mmol) and barbituric acid (67.4 mg, 0.526 mmol) in EtOH (20 mL) was refluxed for 2.5 h. The reaction mixture was cooled to r.t., and the resulting precipitates were collected by filtration and washed with EtOH to give nearly pure compound **1-BDT** as a black-purple solid (71.9 mg, 57%). This compound was further purified by preparative

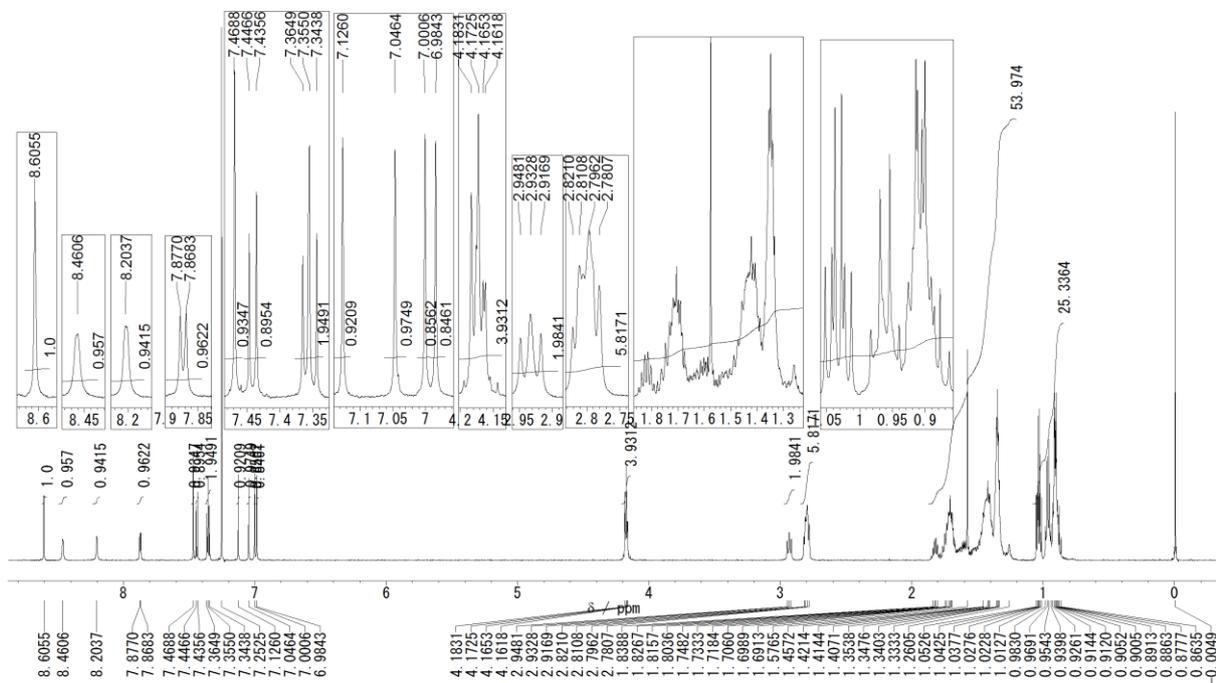
gel permeation chromatography (GPC) using  $\text{CHCl}_3$  as eluent.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , 293 K):  $\delta$  = 8.61 (s, 1H), 8.46 (br-s, 1H), 8.20 (br-s, 1H), 7.87 (d,  $J$  = 4.4 Hz, 1H), 7.47 (s, 1H), 7.44 (d,  $J$  = 5.5 Hz, 1H), 7.36 (d,  $J$  = 4.4 Hz, 1H), 7.35 (d,  $J$  = 5.5 Hz, 1H), 7.13 (s, 1H), 7.05 (s, 1H), 7.00 (s, 1H), 6.98 (s, 1H), 4.18–4.16 (m, 4H), 2.93 (t,  $J$  = 7.8 Hz, 2H), 2.82–2.78 (m, 6H), 1.84–1.26 (m, 50H), 1.05–0.86 (m, 24H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ , 293 K):  $\delta$  = 164.02, 162.49, 154.89, 149.88, 148.04, 147.20, 144.71, 144.56, 144.27, 141.13, 140.41, 140.21, 138.10, 136.26, 135.79, 134.93, 134.84, 133.91, 132.17, 131.89, 131.02, 130.53, 130.48, 129.94, 129.83, 128.94, 128.70, 128.52, 128.34, 125.99, 120.46, 118.67, 115.82, 107.22, 76.08, 76.05, 40.81, 31.89, 31.85, 30.70, 30.61, 30.54, 30.48, 30.37, 30.07, 29.95, 29.81, 29.78, 29.49, 29.40, 29.35, 24.00, 23.98, 23.37, 23.30, 22.84, 14.42, 14.35, 14.30, 11.50; HRMS (APCI):  $m/z$  calcd for  $\text{C}_{75}\text{H}_{99}\text{O}_5\text{N}_2\text{S}_7$  1331.5593  $[\text{M}+\text{H}]^+$ , found 1331.5623; IR (KBr): 3395, 2957, 2930, 2872, 2859, 1741, 1715, 1671, 1552, 1390, 1220, 1088  $\text{cm}^{-1}$ .



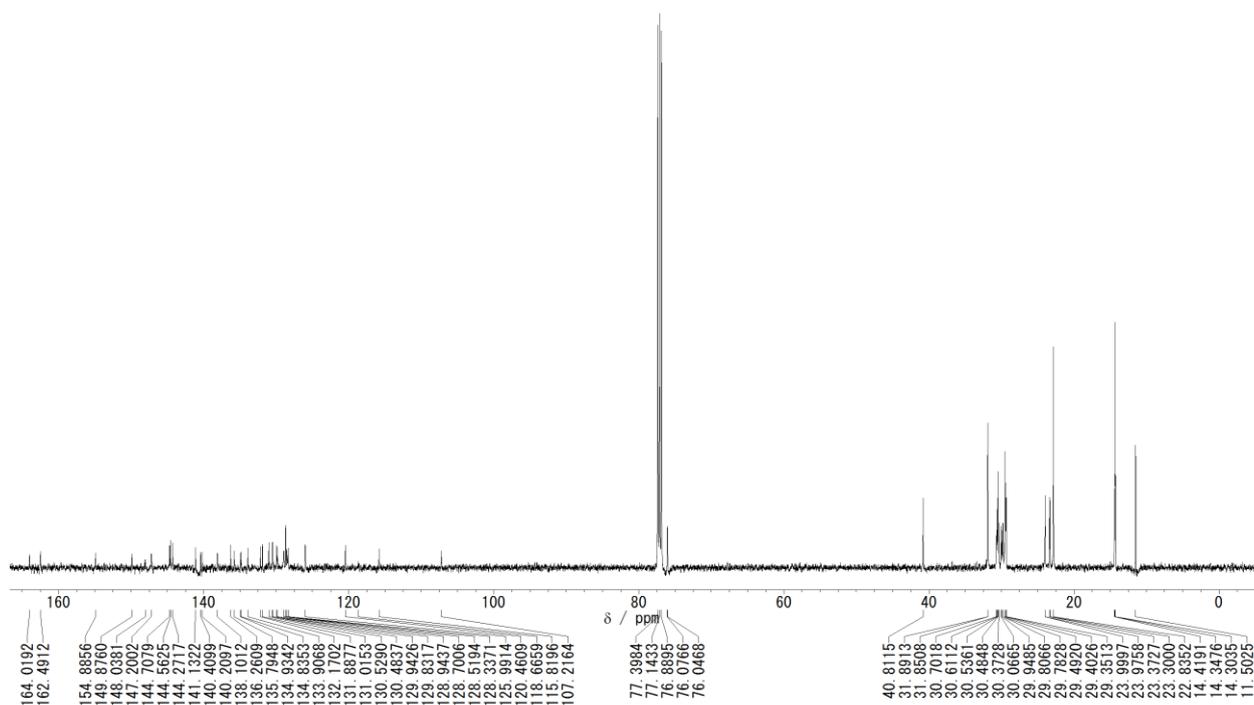
**Fig. S1**  $^1\text{H}$  NMR spectrum of **5** in  $\text{CDCl}_3$  at 293 K.



**Fig. S2**  $^{13}\text{C}$  NMR spectrum of **5** in  $\text{CDCl}_3$  at 293 K.

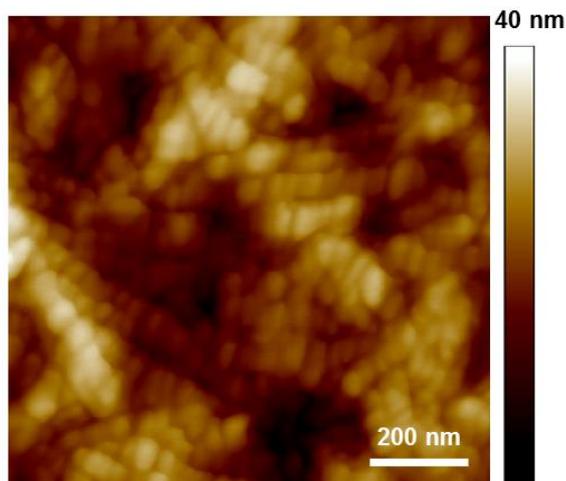


**Fig. S3**  $^1\text{H}$  NMR spectrum of **1-BDT** in  $\text{CDCl}_3$  at 293 K.

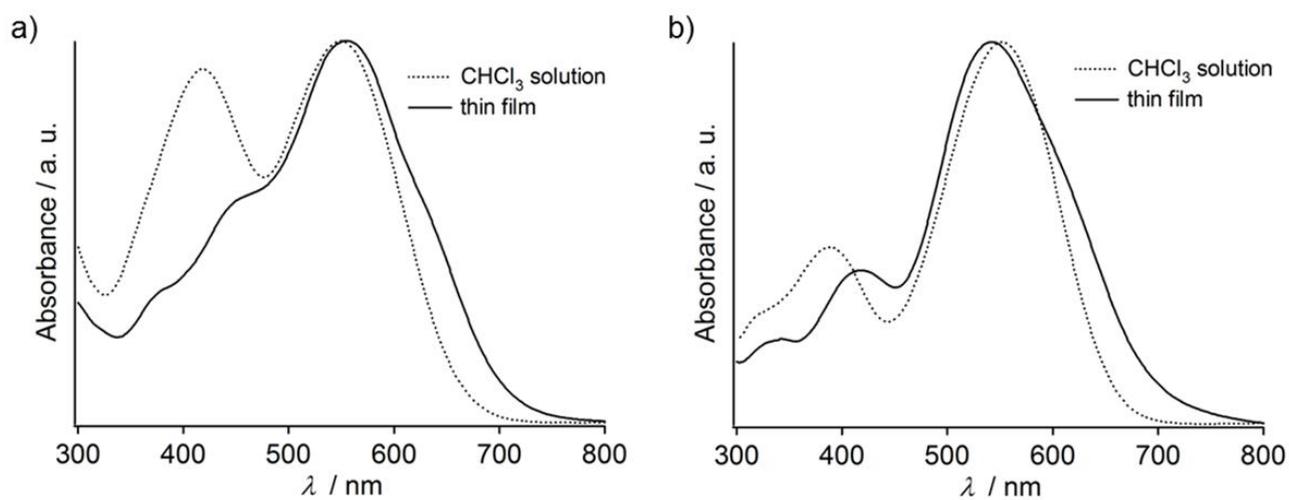


**Fig. S4**  $^{13}\text{C}$  NMR spectrum of **1-BDT** in  $\text{CDCl}_3$  at 293 K.

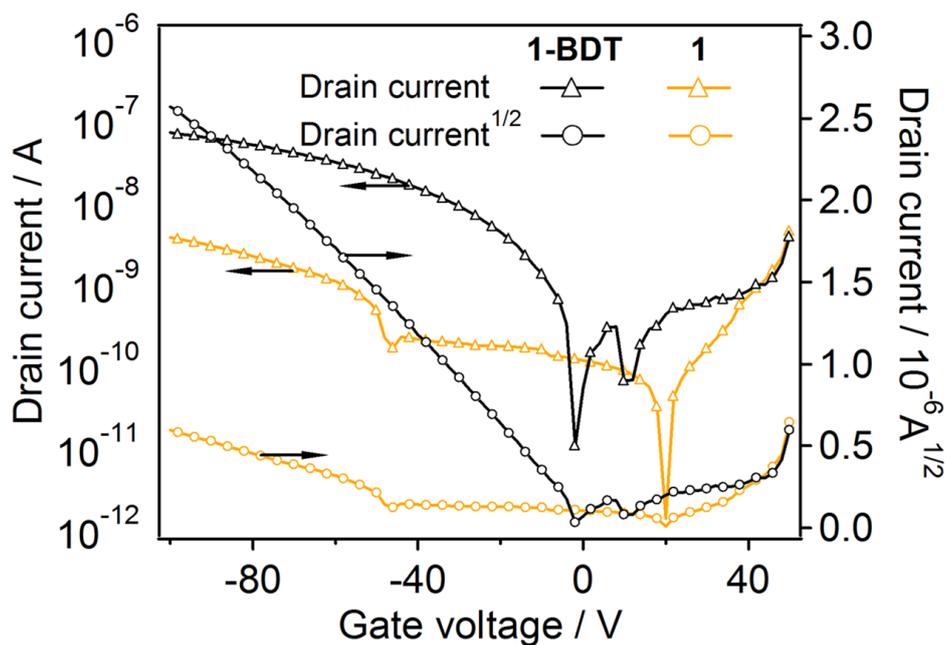
## Supporting Figures



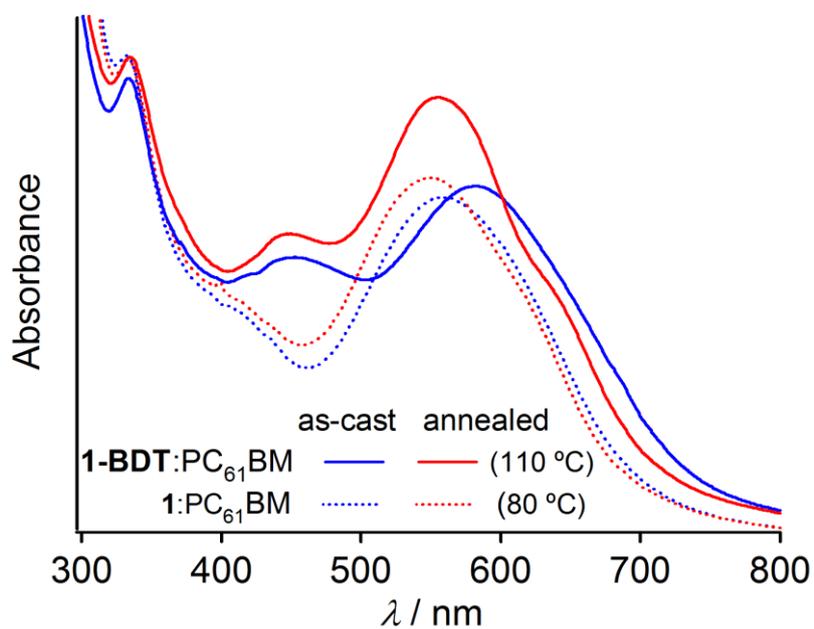
**Fig. S5** AFM image of **1-BDT** films prepared by spin-coating a chloroform gel ( $c = 2 \times 10^{-2}$  M) onto HOPG.



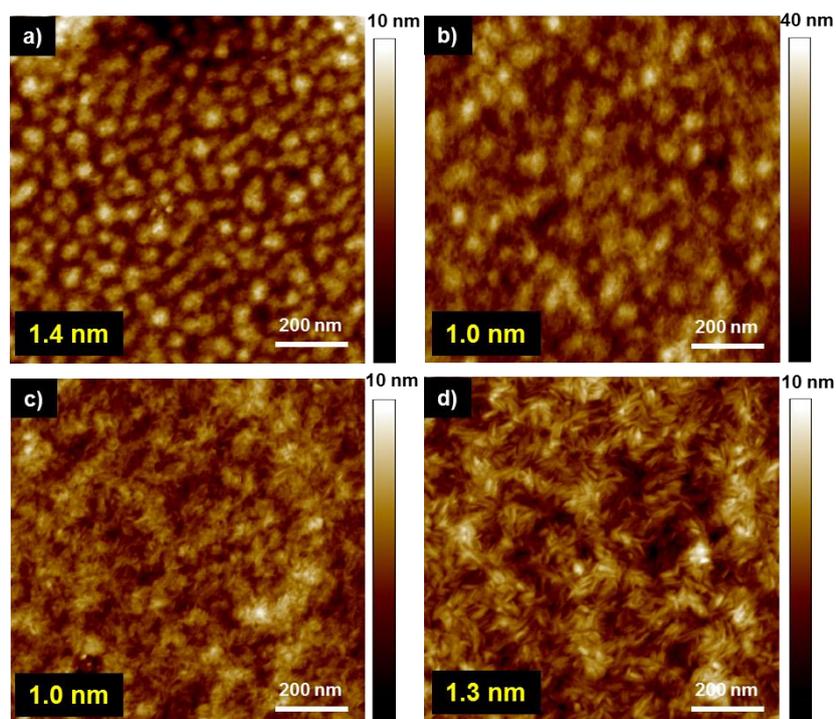
**Fig. S6** Normalised UV-vis absorption spectra of a) **1-BDT** and b) **1** in  $\text{CHCl}_3$  (dashed curves,  $c = 1 \times 10^{-5}$  M) and in thin films (solid curves).



**Fig. S7** Transfer characteristics of the OFET devices of **1-BDT** and **1**.



**Fig. S8** UV-vis spectra of thin films of **1-BDT:PC<sub>61</sub>BM** (solid lines) and **1:PC<sub>61</sub>BM** (dotted lines) before (blue) and after annealing (red). Film thickness: 100–120 nm.



**Fig. S9** AFM images of **1-BDT:PC<sub>61</sub>BM** films prepared by spin-coating a chloroform solution (10 mg mL<sup>-1</sup>) before and after annealing. a) as-cast, b) 50 °C, c) 80 °C, and d) 110 °C. The values at the left-bottom corner are root-mean-square (RMS) roughness. Film thickness: 100–120 nm.

**Table S1** OFET properties of **1-BDT** and **1**.

Compound	hole mobility (cm <sup>2</sup> /Vs)	On/Off	V <sub>th</sub> (V) <sup>a</sup>
<b>1-BDT</b>	1.24x10 <sup>-5</sup>	1.9x10 <sup>3</sup>	-1.79
<b>1</b> <sup>b</sup>	~10 <sup>-7</sup>	—	—

<sup>a</sup> Threshold voltage.

<sup>b</sup> Because compound **1** has a very low hole mobility close to instrument detection limit, its on/off ratio and V<sub>th</sub> could not be determined accurately.

## References

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