Supporting Information

Impact of Helical Organization on Photovoltaic Properties of Oligothiophene Supramolecular Polymers

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1. General

Materials and Methods

Column chromatography was performed using 63–210 µm silica gel. Preparative gel permeation chromatography (GPC) was performed on a recycling preparative HPLC (LC-9225NEXT, Japan Analytical Industry) equipped with GPC columns JAIGEL-1H + 2H). 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. ¹H and ¹³C NMR spectra were recorded on Bruker DPS300 and JEOL JNM-ECA500 NMR spectrometers and chemical shifts are reported in ppm (δ) with the signal of TMS as internal standard. APCI- and ESI-MS spectra were measured on an Exactive (Thermo Fisher). Elemental analysis was performed in Chemical Analysis Center in Chiba University. TEM observation was performed on JEM-2100F (JEOL) at acceleration voltage at 120 kV. The sample was prepared by spin-coating assembly solution onto carbon-coated formvar copper grid (200 mesh) and dried under vacuum for 24 h. AFM images were acquired under ambient conditions using Multimode 8 Nanoscope V (Bruker AXS) in Peak Force Tapping (Scanasyst) mode. Silicon cantilevers (SCANASYST-AIR) with a spring constant of 0.4 N/m and a 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. 20150068 and 20160027). Molecular mechanics calculations were performed on MacroModel version 10.4 using AMBER* force field. UV-vis spectra were recorded on a JASCO V660 spectrophotometer. Differential scanning calorimetry (DSC) was performed on SII DSC6220.

Scanning tunneling microscopy (STM)

1-Phenyloctane (98%, Aldrich) solutions of **3** and **4** were prepared at different concentrations. 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.¹

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 20 min 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 N₂ glove box, 0.5 mL of chloroform solutions containing PC71BM (2.5 mg, Luminescence Technology Corp., Taiwan Province) and oligothiophene derivatives (2.5 mg) were spin-coated (1000 rpm for 30 s) onto the substrate. The thicknesses of the resulting BHJ films were determined to be 90-120 nm for 3:PC71BM and 160–280 nm for 4:PC71BM, respectively, by DEKTAK surface profiler (Bruker AXS). Solvent vapor annealing (SVA) was conducted according to the method reported in the following reference: K. Sun, Z. Xiao, S. Lu, W. Zajaczkowski, W. Pisula, E. Hanssen, J. M. White, R. M. Williamson, J. Subbiah, J. Ouyang, et al., Nat. Commun. 2015, 6, 6013. 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 cm². 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 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.

Hole mobility measurements

Hole mobilities of **3**:PC₇₁BM and **4**:PC₇₁BM (prepared from 10 mg mL⁻¹ CHCl₃ solutions) without and with SVA using CS₂ were estimated by the charge-only space-charge limited current (SCLC) method. The SCLC is described by $J = 9\varepsilon_0\varepsilon_r\mu V^2/8L^3$, where J is the current density, L is the film thickness of the active layer, μ is the hole mobility, ε_r is the relative dielectric constant of the transport medium, ε_0 is the permittivity of free space (8.85 × 10⁻¹² F m⁻¹), V is the applied voltage to the device. SCLC measurements were carried out with a device structure of ITO/MoO₃/active layer/MoO₃/Al by taking the current density in the range 0–10 V and fitting the results to a space-charge limited form.

2. Synthesis and Analytical Data

Compound **3** and **4** were synthesized according to Scheme S1. The syntheses of reference compounds **1** and **2** were reported previously.^{2,3}



Scheme S1. Synthesis of 3 and 4. i) LDA, SnBu₃Cl, THF, $-78 \degree C \rightarrow r.t.$; ii) NBS, CHCl₃/acetic acid, $0 \degree C \rightarrow r.t.$; iii) [Pd(PPh₃)₄], DMF, microwave, 150 °C; iv) 5-formylthiophene-2-boronic acid, K₂CO₃, Pd(dppf)Cl₂, toluene/MeOH, 80 °C; v) 5-bromothiophene-2-carbaldehyde, [Pd(PPh₃)₄], DMF, microwave, 150 °C; vi) barbituric acid, EtOH, reflux.

Tributyl(3,4'-dibutyl-[2,2'-bithiophen]-5-yl)stannane (6): To a dry THF (50 mL) solution of **5** (1.25 g, 4.52 mmol) cooled to -78 °C, a hexane/THF solution of lithium diisopropylamide (1.13 M, 4 mL, 4.52 mmol) was dropped over 10 min and the mixture was stirred at -78 °C for 1 h under N₂ atmosphere. After 1 h, SnBu₃Cl (1.50 g, 4.61 mmol) was added and the mixture was stirred for 30 min. The reaction mixture was warmed to r.t., and further stirred overnight. The reaction mixture was poured into water, and evaporated to remove THF. The resulting mixture was extracted by CHCl₃, and washed twice with water. The organic layer was dried with Na₂SO₄, filtered and evaporated to dryness to give compound **6** as light yellow liquid (2.49 g). This compound was used for the following reaction without purification.

5'-Bromo-3,4'-dibutyl-2,2'-bithiophene (**7**): To an ice-cooled 2:1 CHCl₃/acetic acid mixture (30 mL) containing **5** (750 mg, 2.69 mmol), *N*-bromosuccinimide (478 mg, 2.69 mmol) was added in three portions at interval of 10 min. The reaction mixture was warmed to r.t. and stirred for 3 h. The resulting mixture was diluted with CHCl₃, and washed twice with sat. aq. NaHCO₃. The organic layer was dried with Na₂SO₄, filtered and evaporated to dryness to give compound **7** as light yellow liquid (934 mg, 97%). ¹H NMR (300 MHz, CDCl₃, 293 K): δ = 7.16 (d, *J* = 5.2 Hz, 1H), 6.91 (d, *J* = 5.2 Hz, 1H), 6.79 (s, 1H), 2.71 (t, *J* = 7.7 Hz, 2H), 2.61 (t, *J* = 7.7 Hz, 2H), 1.65–1.54 (m, 4H), 1.44–1.32 (m, 4H), 0.97–0.90 (m, 6H); HRMS (APCI): *m*/*z* calcd. for C₁₆H₂₂BrS₂ 357.0341 [M+H]⁺, found 357.0335.

3,4',4'',4'''-Tetrabutyl-2,2':5',2'':5'',2'''-quaterthiophene (8): A 5-mL of microwave reactor vessel was charged with **6** (2.04 g, 3.59 mmol), **7** (865 mg, 2.42 mmol), Pd(PPh₃)₄ (45.6 mg, 0.0395 mmol) and DMF (3 mL), and the vessel was placed into a microwave reactor. The reaction temperature and period were 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 Na₂SO₄, filtered and evaporated to dryness. The resulting liquid was purified by column chromatography (10 w/w% K₂CO₃-silica gel, eluent: hexane) to give pure compound **8** as yellow liquid (1.23 g, 92%). ¹H NMR (300 MHz, CDCl₃, 293 K): δ = 7.16 (d, J = 5.2 Hz, 1H), 6.97 (s, 1H), 6.95 (s, 1H), 6.94 (s, 1H), 6.93 (d, J = 5.2 Hz, 1H), 6.90 (s, 1H), 2.81–2.73 (m, 6H), 2.62 (t, J = 7.7 Hz, 2H), 1.72–1.58 (m, 8H), 1.49–1.33 (m, 8H), 0.98–0.92 (m, 12H); HRMS (ESI): m/z calcd. for C₃₂H₄S4 555.2242 [M+H]⁺, found 555.2235.

5'''-Bromo-3,4',4'',4'''-tetrabutyl-2,2':5',2'':5'',2'''-quaterthiophene (9): To an ice-cooled 2:1 CHCl₃/acetic acid mixture (30 mL) containing **8** (885 mg, 1.59 mmol), *N*-bromosuccinimide (283 mg, 1.59 mmol) was added in three portions with interval of 10 min. The mixture was warmed to r.t. and stirred for 3 h. The reaction mixture was diluted with CHCl₃, washed twice with sat. aq. NaHCO₃. The organic layer was dried with Na₂SO₄, filtered and evaporated to dryness. The residual liquid was purified by column chromatography (silica gel, eluent: hexane) to give pure compound **9** as yellow liquid (727 mg, 72%). ¹H NMR (300 MHz, CDCl₃, 293 K): δ = 7.15 (d, *J* = 5.2 Hz, 1H), 6.94 (s, 1H), 6.93 (s, 1H), 6.92 (d, *J* = 5.2 Hz, 1H), 6.82 (s, 1H), 2.81–2.69 (m, 6H), 2.57 (t, *J* = 7.7 Hz, 2H), 1.71–1.55 (m, 8H), 1.49–1.35 (m, 8H), 0.98–0.92 (m, 12H); HRMS (APCI): *m/z* calcd. for C₃₂H₄₂BrS₄ 633.1347 [M+H]⁺, found 633.1339.

Tributyl(3,4',4'',4'''-tetrabutyl-[2,2':5',2'':5'',2'''-quaterthiophen]-5-yl)stannane (10): To a dry THF (30 mL) solution of **8** (630 mg, 1.14 mmol) cooled to -78 °C, a hexane/THF solution of lithium diisopropylamide (1.13 M, 1.3 mL, 1.47 mmol) was dropped over 10 min and the mixture

was stirred at -78 °C for 1 h under N₂ atmosphere. After 1 h, SnBu₃Cl (405 mg, 1.24 mmol) was added and the mixture was stirred for 30 min. The reaction mixture was warmed to r.t., and further stirred overnight. The reaction mixture was poured into water, and evaporated to remove THF. The resulting mixture was extracted by CHCl₃, and washed twice with water. The organic layer was dried with Na₂SO₄, filtered and evaporated to dryness to give compound **10** as yellow liquid (2.49 g). This compound was used for the following reaction without purification.

3',3'',3''',3''''-Tetrabutyl-[2,2':5',2'':5'',2'':5''',2'''-quinquethiophene]-5-carbaldehyde (11): To a mixture of **9** (892 mg, 1.40 mmol) and 5-formylthiophene-2-boronic acid (438 mg, 2.80 mmol) in 1:1 toluene/methanol mixture (20 mL), Pd(dppf)Cl₂ (52.0 mg, 0.0710 mmol), K₂CO₃ (976 mg, 7.07 mmol) were added and the resulting mixture was stirred at 80 °C for 11 h under N₂ atmosphere. The reaction mixture was cooled to r.t., diluted with ethyl acetate, and then washed twice with water. The organic layer was dried with Na₂SO₄, filtered and evaporated to dryness. The residual liquid was purified by column chromatography (silica gel, eluent: CHCl₃/hexane = 1:1 (v/v)) to give pure compound **11** as orange liquid (478 mg, 51%). ¹H NMR (500 MHz, CDCl₃ 293 K): δ = 9.88 (s, 1H), 7.70 (d, *J* = 3.9 Hz, 1H), 7.24 (d, *J* = 3.9 Hz, 1H), 7.16 (d, *J* = 5.1 Hz, 1H), 7.01 (s, 1H), 6.97 (s, 1H), 6.95 (s, 1H), 6.93 (d, *J* = 5.2 Hz, 1H), 2.85–2.78 (m, 8H), 1.73–1.62 (m, 8H), 1.50–1.38 (m, 8H), 0.99–0.94 (m, 12H); ¹³C NMR (125 MHz, CDCl₃, 293 K): δ = 182.68, 146.32, 142.62, 142.15, 140.70, 140.08, 139.74, 137.04, 136.31, 134.62, 134.46, 130.51, 130.15, 129.71, 129.33, 129.00, 128.89, 128.76, 125.91, 123.79, 33.95, 32.78, 32.75, 32.53, 29.65, 29.38, 29.30, 29.15, 22.82, 14.12; HRMS (ESI): *m/z* calcd for C₃₇H₄₄OS₅ 665.2068 [M+H]⁺, found 665.2063.

4',4'',4''',4''''-Tetrabutyl-[2,2':5',2'':5'',2'':5''',2''':5''',2''''-quinquethiophene]-5-carbaldehyde (12): A 5-mL of microwave reactor vessel was charged with **10** (942 mg, 1.12 mmol), 5-bromothiophene-2-carbaldehyde (156 mg, 0.817 mmol), Pd(PPh₃)₄ (27.0 mg, 0.0234 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 15 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 Na₂SO₄, filtered and evaporated to dryness. The resulting liquid was purified by column chromatography (silica gel, eluent: CHCl₃/hexane = 1:1 (v/v)) to give pure compound **12** as orange liquid (219 mg, 40%). ¹H NMR (500 MHz, CDCl₃ 293 K): δ = 9.84 (s, 1H), 7.65 (d, *J* = 3.9 Hz, 1H), 7.20 (d, *J* = 3.9 Hz, 1H), 7.18 (s, 1H), 7.00 (s, 1H), 6.98 (s, 1H), 6.97 (s, 1H), 6.90 (s, 1H), 2.80–2.75 (m, 6H), 2.64–2.61 (t, *J* = 7.7 Hz, 2H), 1.70–1.61 (m, 8H), 1.48–1.36 (m, 8H), 0.99–0.94 (m, 12H); ¹³C NMR (125 MHz, CDCl₃, 293 K): δ = 182.50, 147.11, 143.74, 141.51, 140.70, 139.91, 139.69, 137.56, 135.45, 133.24, 133.21, 132.94, 132.89, 131.56, 131.43, 129.31, 129.26, 128.79, 127.34, 124.01, 120.22, 33.95, 32.88, 32.80, 32.70, 30.31, 29.24, 29.12, 22.79, 22.53, 14.10; HRMS

(ESI): *m/z* calcd for C₃₇H₄₄OS₅ 665.2068 [M+H]⁺, found 665.2068.

Compound 3: A mixture of **11** (154 mg, 0.231 mmol) and barbituric acid (158 mg, 1.23 mmol) in EtOH (3 mL) was refluxed for 4 h. The reaction mixture was cooled to r.t., and the resulting precipitates were collected by filtration and washed with hot water to give nearly pure compound **3** as a black-purple solid (38.0 mg, 21%). This compound was further purified by preparative gel permeation chromatography (GPC) using CHCl₃ as eluent. ¹H NMR (500 MHz, CDCl₃, 293 K): δ = 8.61 (s, 1H), 8.55 (br-s, 1H), 8.29 (br-s, 1H), 7.88 (d, *J* = 4.2 Hz, 1H), 7.37 (d, *J* = 4.2 Hz, 1H), 7.17 (d, *J* = 5.2 Hz, 1H), 7.04 (s, 1H), 6.97 (s, 1H), 6.94 (s, 1H), 6.93 (d, *J* = 5.2 Hz, 1H), 2.94 (t, *J* = 7.7 Hz, 2H), 2.82–2.77 (m, 6H), 1.77–1.63 (m, 8H), 1.52–1.38 (m, 8H), 1.00–0.93 (m, 12H); HRMS (APCI): *m/z* calcd for C₄₁H₄₆O₃N₂S₅ 775.2185 [M+H]⁺, found 775.2167; Elemental analysis: calcd for C₄₁H₄₆O₃N₂S₅ (%): C, 63.53; H, 5.98; N, 3.61. Found: 63.36; H, 5.85; N, 3.61. ¹³C NMR spectrum of this compound could not be measured due to its low solubility.

Compound 4: A mixture of **12** (106 mg, 0.159 mmol) and barbituric acid (106 mg, 0.828 mmol) in EtOH (30 mL) was refluxed for 3 h. The reaction mixture was cooled to r.t., and the resulting precipitates were collected by filtration and washed with hot water to give nearly pure compound **4** as a black-purple solid (94.3 mg, 77%). ¹H NMR (500 MHz, (CD₃)₂SO, 293 K): $\delta = 11.3$ (s, 2H), 8.47 (s, 1H), 8.14 (d, J = 4.2 Hz, 1H), 7.61 (d, J = 4.2 Hz, 1H), 7.60 (s, 1H), 7.22 (s, 1H), 7.22 (s, 1H), 7.13 (s, 1H), 7.08 (s, 1H), 2.94 (t, J = 7.7 Hz, 2H), 2.81–2.72 (m, 6H), 2.59 (t, J = 7.6 Hz, 2H), 1.68–1.55 (m, 8H), 1.44–1.29 (m, 8H), 0.95–0.69 (m, 12H); HRMS (ESI): m/z calcd for C₄₁H₄₆O₃N₂S₅ 775.2185 [M+H]⁺, found 775.2183; Elemental analysis: calcd for C₄₁H₄₆O₃N₂S₅ (%): C, 63.53; H, 5.98; N, 3.61. Found: 62.85; H, 5.81; N, 3.56. ¹³C NMR spectrum of this compound could not be measured due to its very low solubility.



Chart S1. ¹H NMR spectrum of **11** in CDCl₃ at 293 K.



Chart S2 ¹³C NMR spectrum of 11 in CDCl₃ at 293 K.



Chart S3 ¹H NMR spectrum of 12 in CDCl₃ at 293 K.



Chart. S4 ¹³C NMR spectrum of **12** in CDCl₃ at 293 K.



Chart S5. ¹H NMR spectrum of 3 in CDCl₃ at 293 K.



Chart S6 ¹H NMR spectrum of 4 in (CD₃)₂SO at 293 K.

3. Supporting Figures



Fig. S1. (a) AFM image of thin film prepared by drop-casting toluene solution of **4** ($c = 1 \times 10^{-4}$ M) onto HOPG. (b,c) Cross-sectional analysis between (b) red and (c) blue dots (for height) in the image (a).



Fig. S2. DSC profiles (second heating) of 3 (red) and 4 (blue) measured at a scan rate of 3 $^{\circ}$ C/min. All samples were prepared by drop-casting CHCl₃ solutions onto a glass plate to form thin films. After drying at room temperature for 24 h to remove the residual solvent, the films were collected by scratching and transferred to an aluminum sample pan for DSC measurements.



Fig. S3. AFM image of helical fibers formed in **3**:PC₆₁BM film. The film was prepared by spin-coating a chloroform solution of the 1:1 mixture ($c_{\text{total}} = 10 \text{ mg mL}^{-1}$) and thermal annealing the resulting film at 110 °C.



Fig. S4. (a,b) Effect of SVA (0, 40, 80 ad 120 sec) using CS_2 on UV-vis spectra of BHJ solar cells based on (a) **3**:PC₇₁BM and (b) **4**:PC₇₁BM. Film thickness: 90–120 nm for **3**:PC₇₁BM; 160–280 nm for **4**:PC₇₁BM.



Fig. S5. (a,b) PXRD patterns of bulk sample of (a) **3**:PC₇₁BM and (b) **4**:PC₇₁BM in a glass capillary (diameter: 1.0 mm). Values in parenthesis denote Miller indices. The four peaks in small-angle region in (a) can be thus assigned to the diffractions from the (100), (200), (010), and (020) planes of a 2D rectangular lattice (space group: *P2m*, lattice parameters: a = 3.2 nm, b = 1.2 nm), respectively. Likewise, six peaks in small-angle region in (b) can be thus assigned to the diffractions from the (100), (200), (010), (110), (001), and (020) planes of a 2D rectangular lattice (space group: P2m, lattice parameters: a = 3.2 nm, b = 1.2 nm), respectively. Likewise, six peaks in small-angle region in (b) can be thus assigned to the diffractions from the (100), (200), (010), (110), (001), and (020) planes of a 2D rectangular lattice (space group: P2m, lattice parameters: a = 3.2 nm, b = 1.2 nm), respectively.

Note: The sharp diffraction at d = 3.91 nm, which is accompanied by the higher order diffractions at d = 1.98 and 1.30 nm, cannot be assigned at the moment. Because the intensities of these diffraction peaks differ by samples, they do not arise from the structural rearrangement of **4**. They may rather arise from certain ordering of PC₇₁BM upon co-aggregation with highly crystalline **4**.



Fig. S6. (a,b) Normalized UV-vis spectra of thin films of (a) **3** (dashed curve, c = 5 mg mL⁻¹) and **3**:PC₇₁BM (solid curve, $c_{\text{total}} = 10$ mg mL⁻¹), and (b) **4** (dashed curve, c = 5 mg mL⁻¹) and **4**:PC₇₁BM (solid curve, $c_{\text{total}} = 10$ mg mL⁻¹).



Fig. S7. (a,b) Effect of SVA (0, 40, 80 and 120 sec) using CS_2 on EQE spectra of BHJ solar cells based on (a) **3**:PC₇₁BM and (b) **4**:PC₇₁BM.



Fig. S8. (a,b) Effect of SVA (0, 40, 80 and 120 sec) using CS_2 on J-V characteristics of (a) **3**:PC₇₁BM and (b) **4**:PC₇₁BM BHJ solar cells.

4. Supporting Tables

BHJ films	Annealing temp [s]	$J_{\rm sc}$ [mA cm ⁻²]	$V_{ m oc}$ [V]	FF [%]	PCE [%]
3 :PC ₇₁ BM	As-cast	6.63 ± 0.11	0.86 ± 0.02	36.9 ± 0.7	2.10 ± 0.09
	80	5.44 ± 0.09	0.81 ± 0.03	34.0 ± 1.4	1.49 ± 0.14
	110	6.13 ± 0.19	0.71 ± 0.01	36.3 ± 0.4	1.57 ± 0.04
	130	6.13 ± 0.02	0.69 ± 0.01	43.5 ± 0.7	1.82 ± 0.05
4 :PC ₇₁ BM	As-cast	3.53 ± 0.23	0.75 ± 0.01	45.2 ± 0.2	1.19 ± 0.10
	80	3.56 ± 0.14	0.76 ± 0.01	49.3 ± 0.6	1.33 ± 0.06
	110	0.81 ± 0.36	0.74 ± 0.01	41.9 ± 1.1	0.26 ± 0.12
	130	1.12 ± 0.16	0.75 ± 0.01	43.4 ± 2.7	0.36 ± 0.04

Table S1. Effect of thermal annealing on photovoltaic properties of $3:PC_{71}BM$ and $4:PC_{71}BM$ BHJ solar cells.

Table S2. Hole mobilities of $3:PC_{71}BM$ and $4:PC_{71}BM$ without and with SVA (CS₂) evaluated by the charge-only space-charge limited current (SCLC) method.

BHJ films	SVA time [s]	Thickness [nm]	Hole mobility $[cm^2 V^{-1} s^{-1}]$
3 :PC ₇₁ BM	0	115	$6.6 imes 10^{-6}$
	80	107	$1.2 imes 10^{-5}$
4 :PC ₇₁ BM	0	172	$1.2 imes 10^{-3}$
	80	198	$4.3 imes 10^{-3}$

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