

SUPPLEMENTARY INFORMATION

High-fidelity self-assembly pathways for hydrogen-bonding molecular semiconductors

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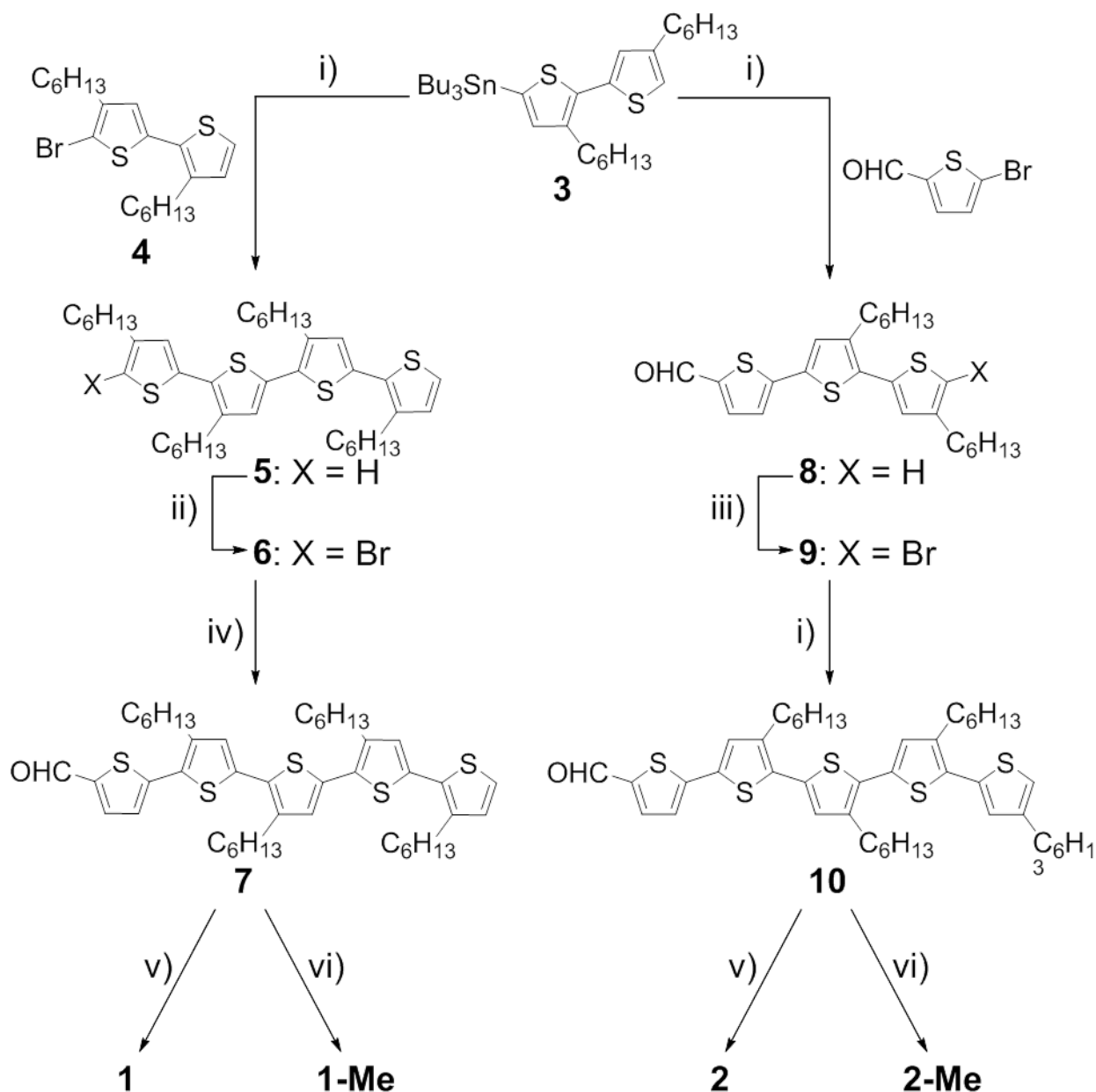
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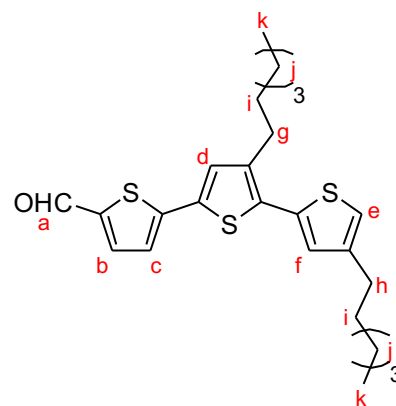
Synthesis and Characterization

Barbiturate-conjugated thienyl[oligohexyl(thiophene)]s **2** and non-hydrogen-bonding derivatives **2-Me** were synthesized according to the following steps. Compounds **1**, **1-Me**, **3**, **4**, **5**, **6** and **7** were synthesized according to Scheme S1 and details were reported previously.^{S1}



i) $\text{Pd}(\text{PPh}_3)_4$, DMF, microwave 140 °C; ii) NBS, CHCl_3 /acetic acid, 0 °C $\rightarrow$ r.t.; iii) NBS, DMF, 0 °C $\rightarrow$ r.t.; iv) 5-formylthiophene-2-boronic acid, K_2CO_3 , $\text{Pd}(\text{dppf})\text{Cl}_2$, toluene/MeOH, 80 °C; v) barbituric acid, EtOH, reflux; vi) 1,3-dimethylbarbituric acid, EtOH, reflux.

Synthesis of compound 8: A 5-mL of microwave reactor vessel was charged with 5-bromothiophene-2-carboxaldehyde (100 mg, 0.52 mmol), **3** (486 mg, 0.78 mmol), Pd(PPh₃)₄ (20 mg, 0.016 mmol), and DMF (3 mL), and the vessel was placed into a microwave reactor. The reaction temperature and period were set to 140 °C and 7 min, respectively. The reaction 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: CHCl₃/hexane = 2:3 (v/v)) to give pure compound **8** as an orange liquid (227 mg, 98%). ¹H NMR (300 MHz, CDCl₃): δ = 9.85 (s, 1H, CH_aO), 7.66 (d, *J* = 4.1 Hz, 1H, thienyl-*H*_b), 7.21 (d, *J* = 3.9 Hz, 1H, thienyl-*H*_c), 7.18 (s, 1H, thienyl-*H*_d), 7.00 (s, 1H, thienyl-*H*_e), 6.94 (s, 1H, thienyl-*H*_f), 2.74 (t, *J* = 7.7 Hz, 2H, CH_g), 2.61 (t, *J* = 7.4 Hz, 2H, CH_h), 1.65–1.54 (m, 4H, CH_i), 1.41–1.32 (m, 12H, CH_j), 0.92–0.87 (m, 6H, CH_k); ¹³C NMR (75.49 MHz, CDCl₃): δ = 182.21, 146.98, 143.79, 141.33, 140.37, 137.36, 134.84, 133.25, 133.03, 128.90, 127.59, 123.78, 120.71, 31.68, 31.61, 30.43, 30.36, 29.31, 29.21, 29.02, 22.63, 22.40, 14.12, 14.09; HRMS (ESI) *m/z* calcd. for C₂₅H₃₃OS₃ 445.1688 [M+H]⁺; found 445.1674.

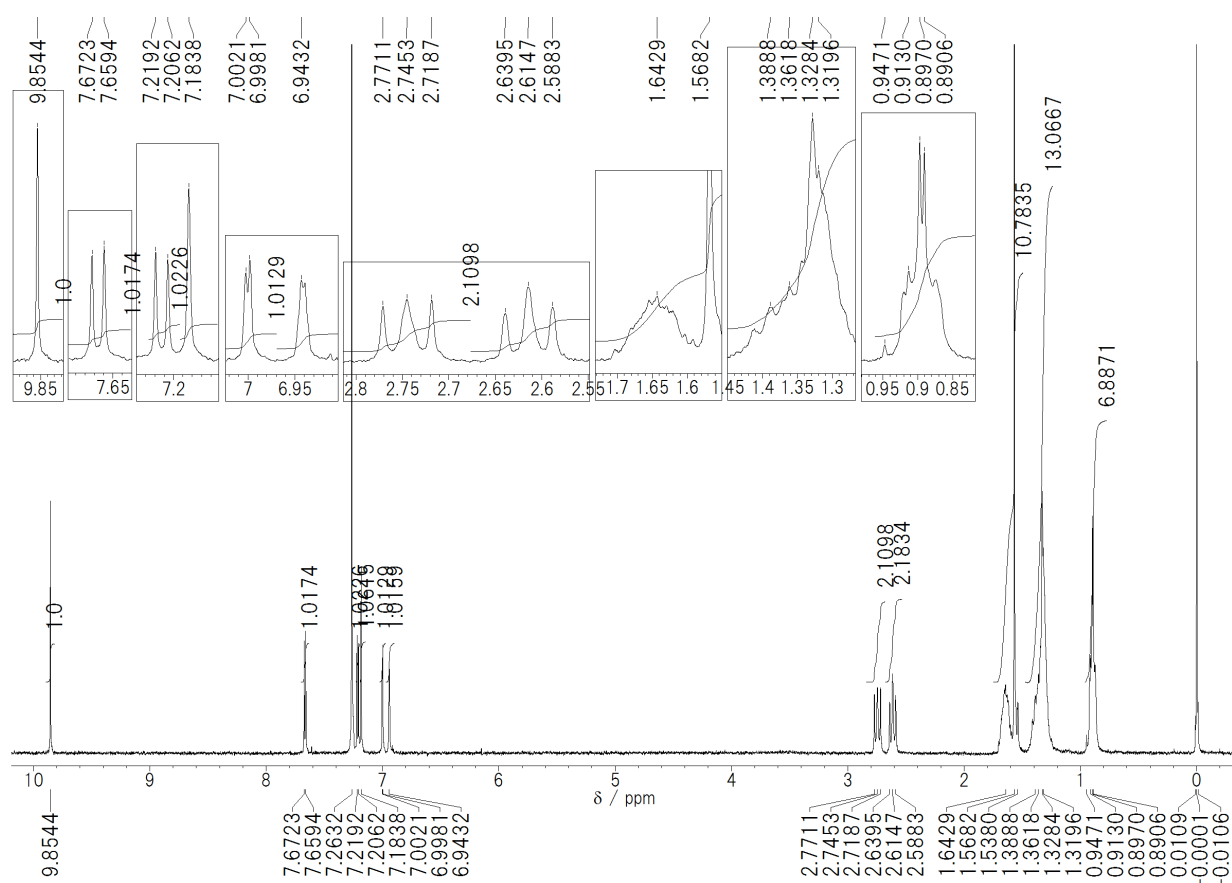


Figure S1. ¹H NMR spectrum of **8** in CDCl₃ at 293 K.

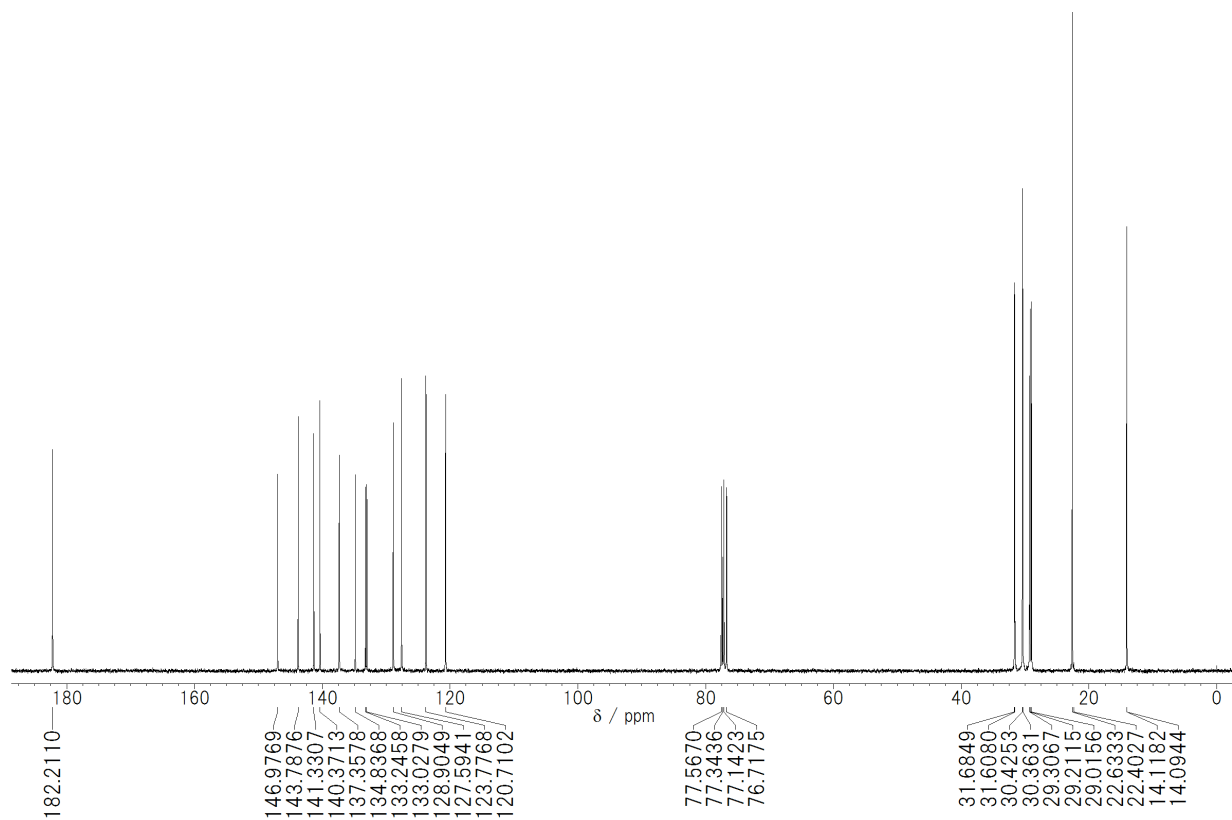
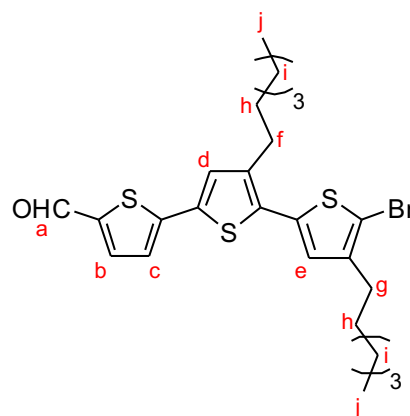


Figure S2. ¹³C NMR spectrum of **8** in CDCl₃ at 293 K.

Synthesis of compound 9: To an ice-cooled DMF solution (10 mL) containing **8** (227 mg, 0.51 mmol), *N*-bromosuccinimide (91 mg, 0.51 mmol) was added in three portions with interval of 10 min. The reaction mixture was warmed to r.t. and stirred overnight. The mixture was diluted with ethyl acetate, and washed twice with water and once with brine. The organic layer was dried over Na₂SO₄, filtered and evaporated to dryness to give compound **9** as an orange liquid in almost quantitative yield without purification (268 mg, 100%). ¹H NMR (300 MHz, CDCl₃): δ = 9.86 (s, 1H, CH_aO), 7.67 (d, *J* = 3.9 Hz, 1H, thienyl-*H*_b), 7.21 (d, *J* = 4.0 Hz, 1H, thienyl-*H*_c), 7.17 (s, 1H, thienyl-*H*_d), 6.85 (s, 1H thienyl-*H*_e), 2.70 (t, *J* = 7.8 Hz, 2H, CH_f), 2.57 (t, *J* = 7.5 Hz, 2H, CH_g), 1.62–1.56 (m, 4H CH_h), 1.33–1.25 (m, 12H, CH_i), 0.92–0.87 (m, 6H CH_j); ¹³C NMR (75.49 MHz, CDCl₃): δ = 182.80, 147.14, 143.07, 141.95, 141.34, 137.85, 135.05, 133.95, 132.49, 129.29, 127.52, 126.77, 124.44, 109.94, 32.02, 30.86, 30.05, 29.92, 29.70, 29.59, 29.33, 23.03, 14.53; HRMS (ESI) *m/z* calcd. for C₂₅H₃₂OBrS₃ 523.0793 [M+H]⁺; found 523.0783.



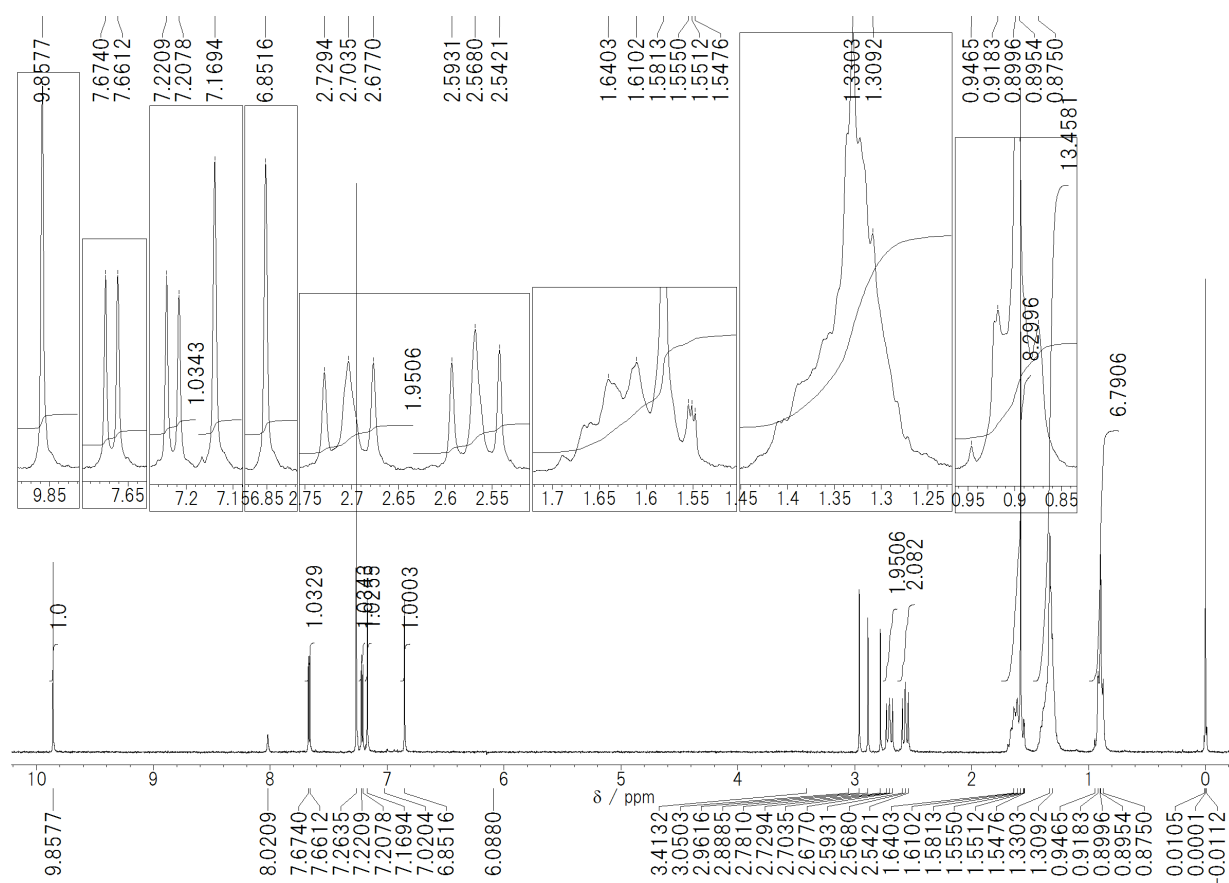


Figure S3. ¹H NMR spectrum of **9** in CDCl₃ at 293 K.

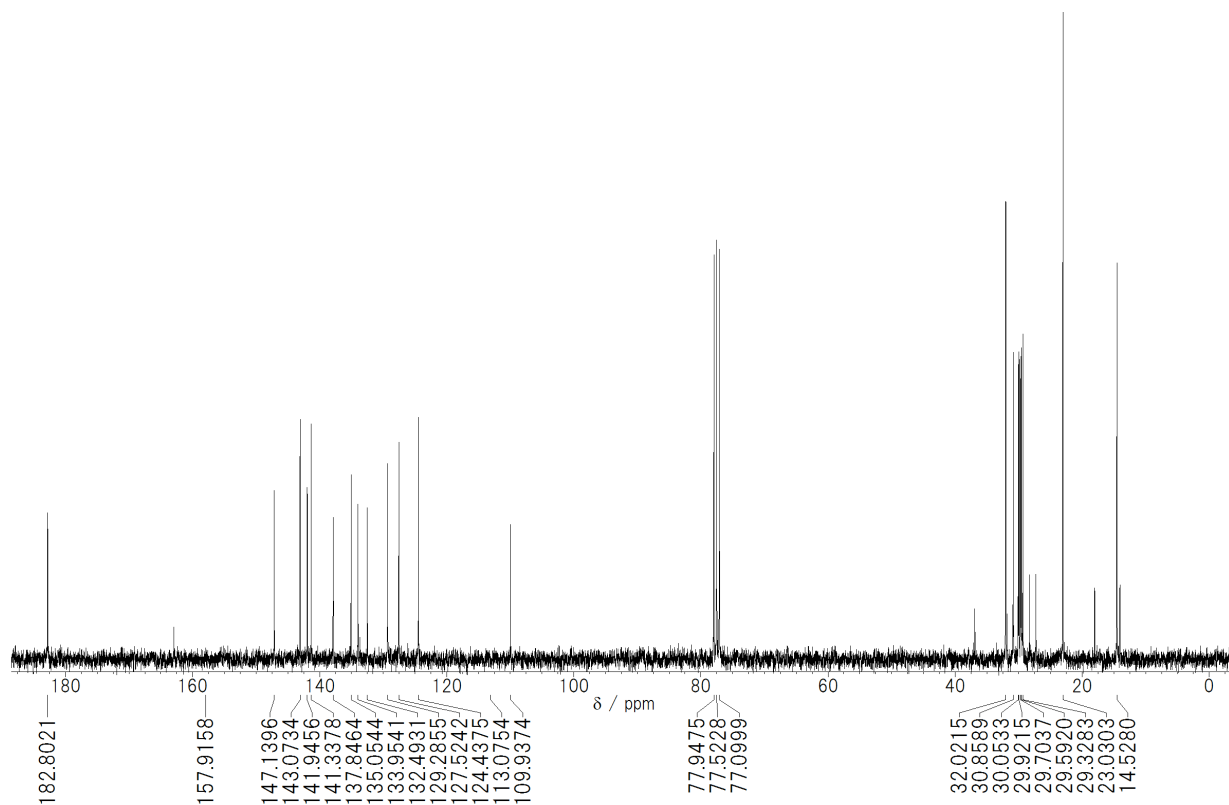
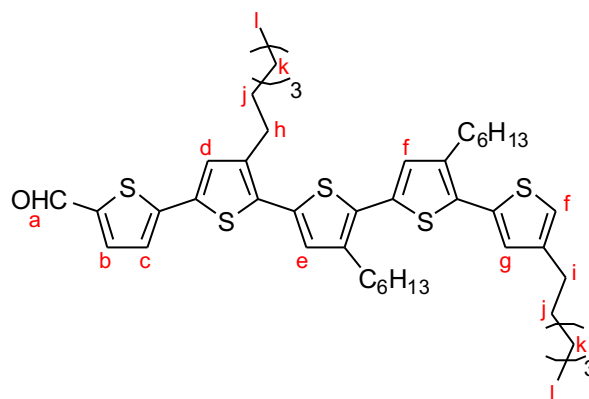


Figure S4. ¹³C NMR spectrum of **9** in CDCl₃ at 293 K.

Synthesis of compound 10: A 5-mL of microwave reactor vessel was charged with **9** (268 mg, 0.51 mmol), **3** (383 mg, 0.61 mmol), Pd(PPh₃)₄ (20 mg, 0.016 mmol), and DMF (3 mL), and the vessel was placed into a microwave reactor. The reaction temperature and period was set to 140 °C and 7 min,



respectively. The reaction 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: CHCl₃/hexane = 2:3 (v/v)) to give pure compound **10** as an orange liquid (263 mg, 56%).

¹H NMR (300 MHz, CDCl₃): δ = 9.86 (s, 1H, CH_aO), 7.67 (d, *J* = 3.9 Hz, 1H, thienyl-*H*_b), 7.22 (d, *J* = 4.0 Hz, 1H, thienyl-*H*_c), 7.19 (s, 1H, thienyl-*H*_d), 7.00 (s, 1H, thienyl-*H*_e), 6.97 (m, 2H, thienyl-*H*_f), 6.91 (s, 1H, thienyl-*H*_g), 2.81–2.73 (m, 6H, CH_h), 2.61 (t, *J* = 7.7 Hz, 2H, CH_i), 1.68–1.60 (m, 8H, CH_j), 1.42–1.25 (m, 24H, CH_k), 0.90–0.89 (m, 12H, CH_l); ¹³C NMR (75.49 MHz, CDCl₃): δ = 182.83, 147.43, 144.11, 141.81, 141.06, 140.27, 140.05, 135.80, 133.54, 133.26, 133.21, 131.88, 131.74, 129.60, 129.46, 129.06, 128.45, 127.61, 125.72, 124.32, 120.53, 32.11, 32.08, 31.01, 30.93, 30.84, 29.91, 29.84, 29.69, 29.47, 23.08, 14.56; HRMS (ESI) *m/z* calcd. for C₄₅H₆₁OS₅ 777.3320 [M+H]⁺; found 777.3301.

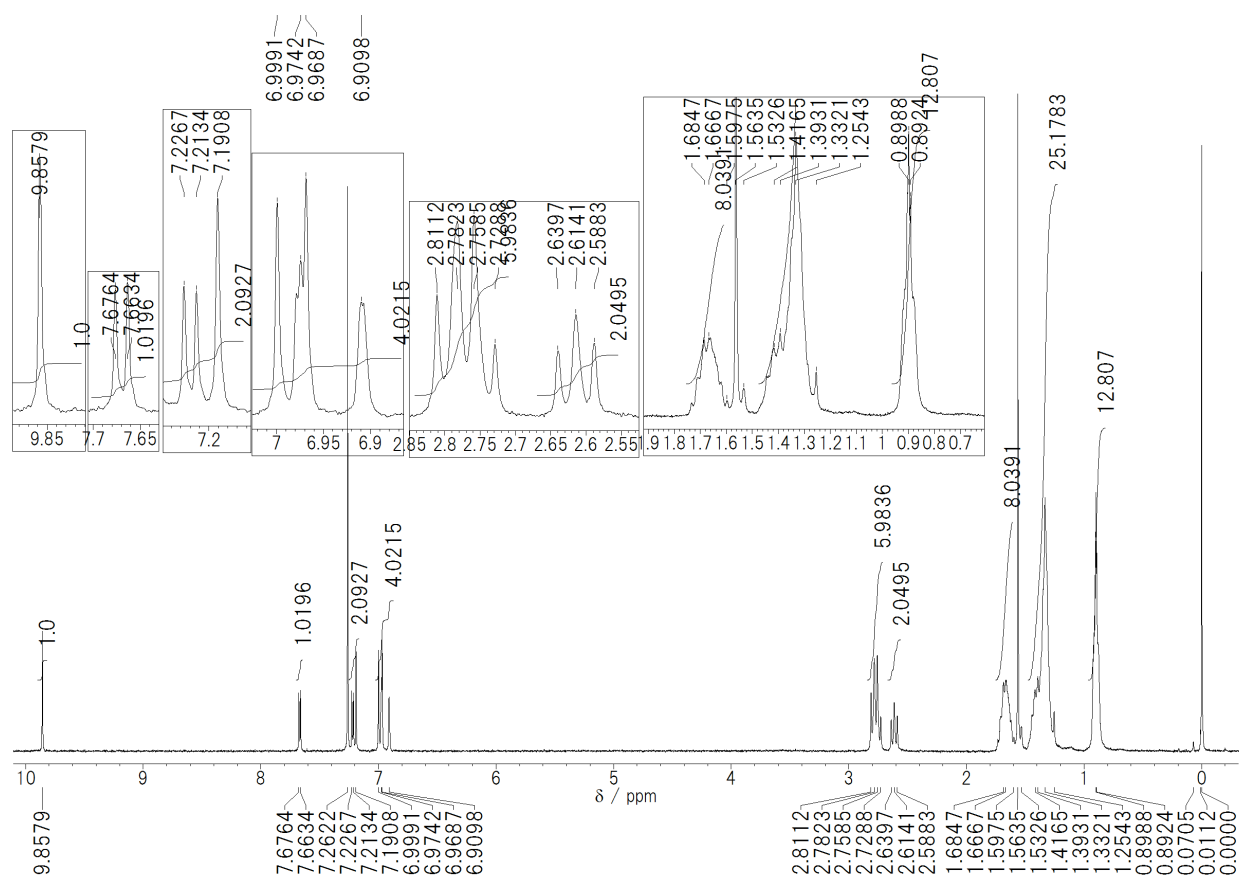


Figure S5. ¹H NMR spectrum of **10** in CDCl₃ at 293 K.

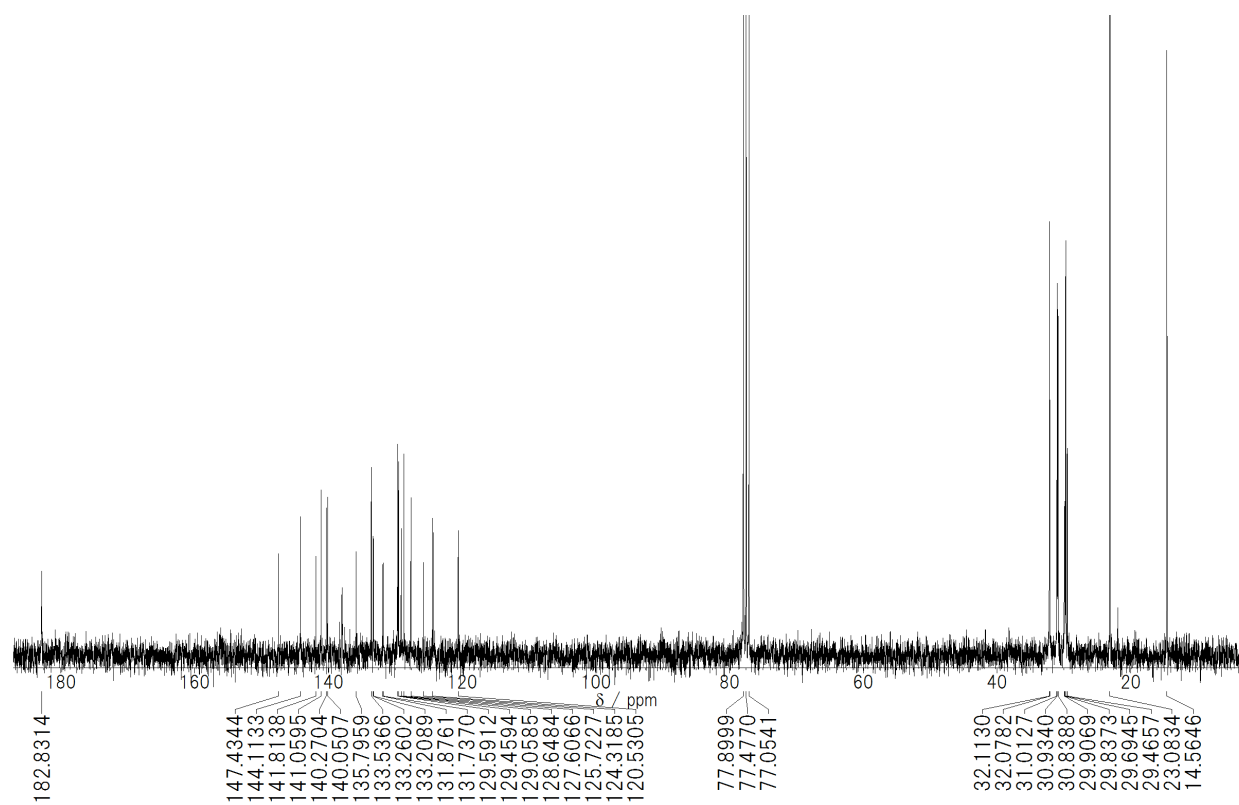


Figure S6. ¹³C NMR spectrum of **10** in CDCl₃ at 293 K.

Synthesis of compound 2: A mixture of **10** (263

mg, 0.34 mmol) and barbituric acid (150 mg,

1.20 mmol) in EtOH (5 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 repeatedly. The

residual solid was reprecipitated from a CHCl₃–hexane mixture to give nearly pure compound **2** as

a black-purple solid (168 mg, 56%). This compound was further purified by preparative GPC

(eluent: CHCl₃). Mp 157 °C (DSC 2nd heating); ¹H NMR (500 MHz, CDCl₃, 60 °C): δ = 8.59 (s,

1H, C=CH_a–thienyl), 8.02 (br-s, 1H, NH_b), 7.99 (br-s, 1H, NH_c), 7.82 (d, *J* = 4.3 Hz, 1H,

thienyl-*H*_d), 7.40 (s, 1H, thienyl-*H*_e), 7.34 (d, *J* = 4.2 Hz, 1H, thienyl-*H*_f), 7.04 (s, 1H, thienyl-*H*_g),

6.98 (m, 2H, thienyl-*H*_h), 6.91 (s, 1H, thienyl-*H*_i), 2.82–2.72 (m, 6H, CH_j), 2.61 (t, *J* = 7.6 Hz, 2H,

CH_k), 1.73–1.62 (m, 8H, CH_l), 1.45–1.28 (m, 24H, CH_m), 0.93–0.86 (m, 12H, CH_n); ¹³C NMR

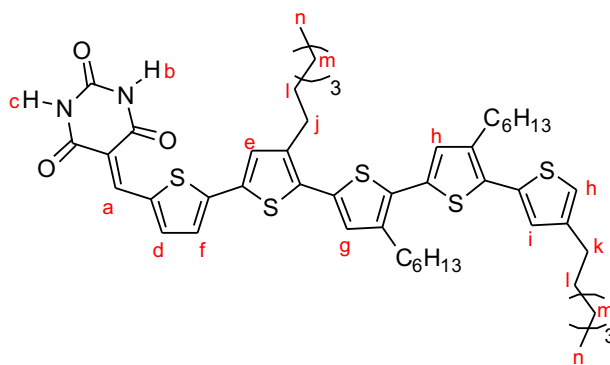
(125.77 MHz, tetrachloroethane-*d*₂, 130 °C): δ = 162.72, 162.01, 154.75, 148.51, 148.18, 147.18,

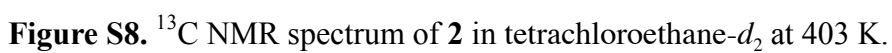
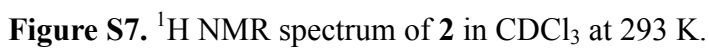
143.83, 141.57, 140.35, 140.01, 135.66, 135.62, 135.14, 133.47, 133.40, 133.02, 132.36, 131.91,

130.51, 129.75, 129.04, 127.64, 124.79, 120.34, 108.14, 31.65, 31.62, 30.72, 30.57, 30.40, 30.36,

30.34, 30.28, 29.66, 29.53, 29.40, 29.17, 29.14, 28.96, 22.51, 13.86; HRMS (ESI) *m/z* calcd. for

C₄₉H₆₃O₃N₂S₅ 887.3437 [M+H]⁺; found 887.3431.





Synthesis of compound 2-Me: A mixture of

10 (81 mg, 0.10 mmol) and

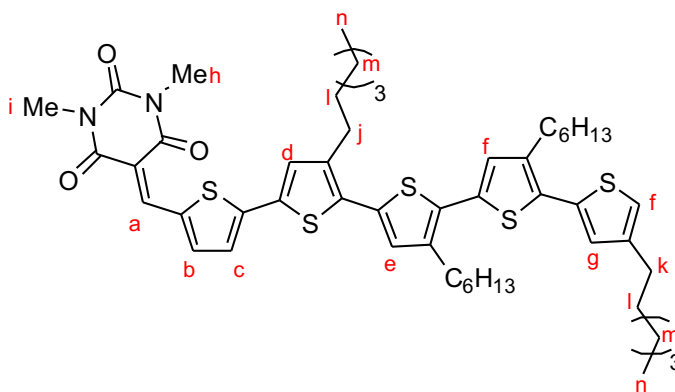
N,N'-dimethylbarbituric acid (70 mg, 0.45 mmol) in EtOH (5 mL) was refluxed for 3 h.

The reaction mixture was cooled to r.t., and

the resulting precipitates were collected by

filtration and washed with hot water repeatedly. The residual solid was reprecipitated from a CHCl₃–EtOH mixture to give nearly pure compound **2-Me** as a black-purple solid (89 mg, 97%).

This compound was further purified by preparative GPC (eluent: CHCl₃). Mp 97 °C (DSC); ¹H NMR (500 MHz, CDCl₃): δ = 8.63 (s, 1H, C=CH_a–thienyl), 7.78 (d, *J* = 4.4 Hz, 1H, thienyl-*H*_b), 7.40 (s, 1H, thienyl-*H*_c), 7.32 (d, *J* = 4.3 Hz, 1H, thienyl-*H*_d), 7.03 (s, 1H, thienyl-*H*_e), 6.98 (s, 2H, thienyl-*H*_f), 6.91 (s, 1H, thienyl-*H*_g), 3.45 (s, 3H, N–CH_h), 3.43 (s, 3H, N–CH_i), 2.82–2.73 (m, 6H, CH_j), 2.62 (t, *J* = 7.6 Hz, 2H, CH_k), 1.73–1.60 (m, 8H, CH_l), 1.46–1.28 (m, 24H, CH_m), 0.93–0.87 (m, 12H, CH_n); ¹³C NMR (75.49 MHz, CDCl₃): δ = 163.18, 162.56, 153.98, 151.85, 148.59, 147.58, 144.11, 141.45, 140.35, 140.08, 135.76, 135.75, 134.69, 133.66, 133.47, 133.17, 132.21, 131.84, 130.60, 129.76, 129.12, 127.64, 124.77, 120.55, 108.95, 32.07, 30.97, 30.90, 30.88, 30.81, 30.78, 29.98, 29.80, 29.67, 29.64, 29.42, 29.29, 28.55, 23.04, 14.52; HRMS (ESI) *m/z* calcd. for C₅₁H₆₇O₃N₂S₅ 915.3750 [M+H]⁺; found 915.3740.



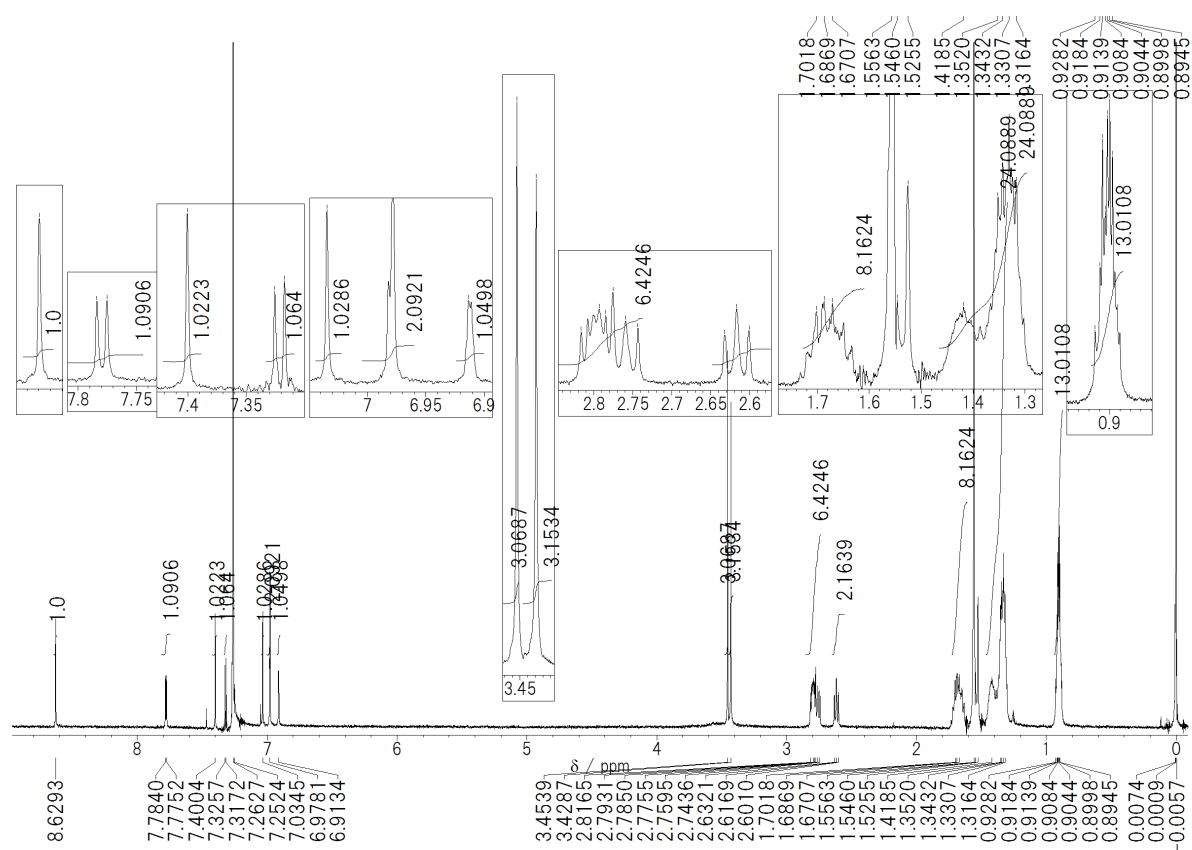


Figure S9. ¹H NMR spectrum of **2-Me** in CDCl₃ at 293 K.

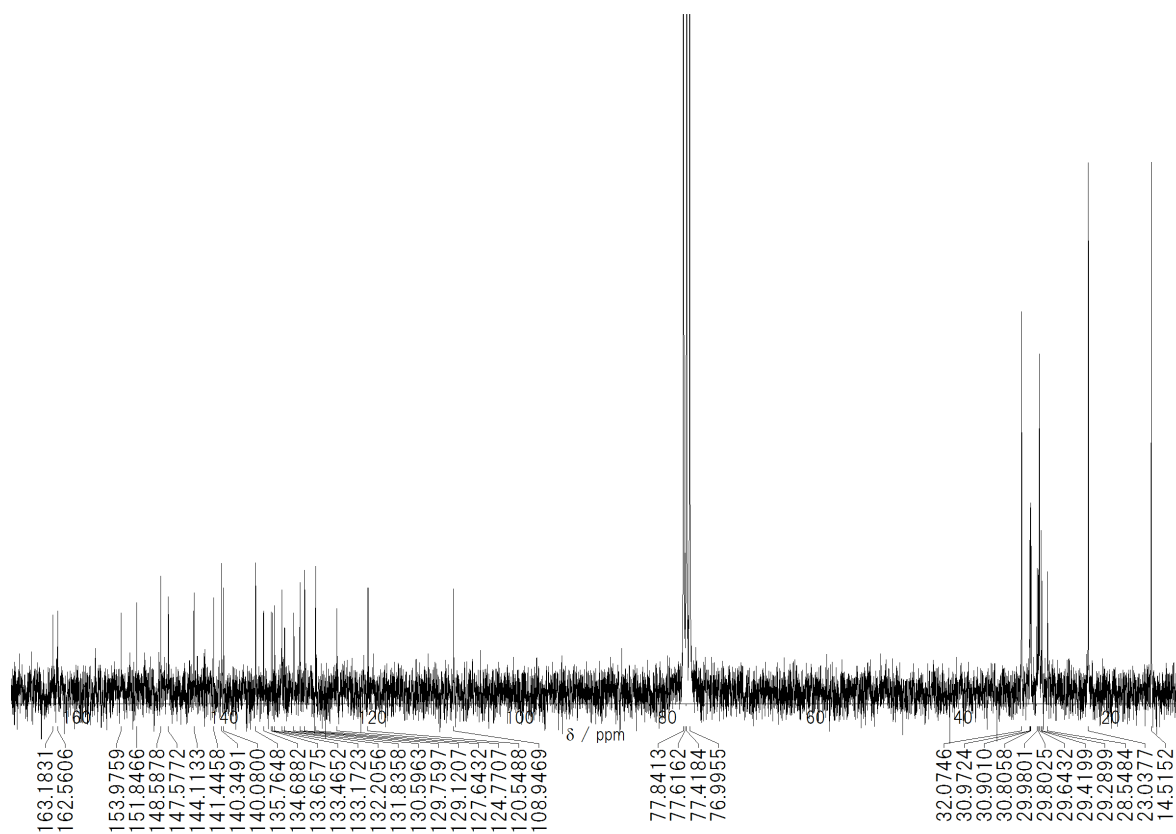


Figure S10. ¹³C NMR spectrum of **2-Me** in CDCl₃ at 293 K.

Supplementary Data

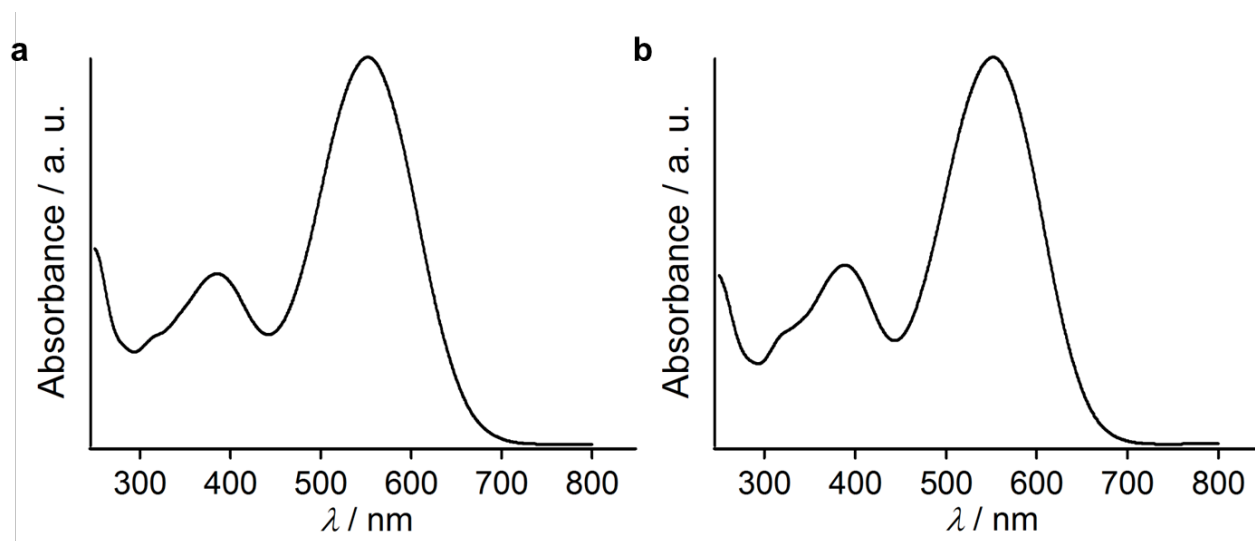


Figure S11. UV-vis absorption spectra of **1(a)** and **2(b)** ($c = 0.01$ mM) in CHCl_3 .

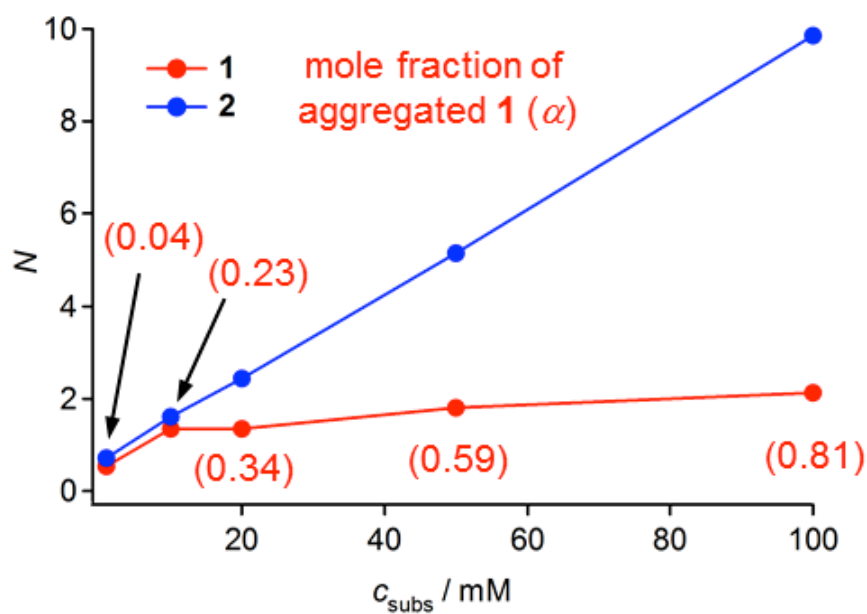


Figure S12. VPO-derived plots of the aggregation number $N = c_{\text{subs}}/c_{\text{collig}}$ (c_{mon} : 10 – 100 mM) as a function of the monomer concentration of **1** (red) and **2** (blue). Numbers in parentheses indicate the fraction of aggregated molecules (α) of **1**.

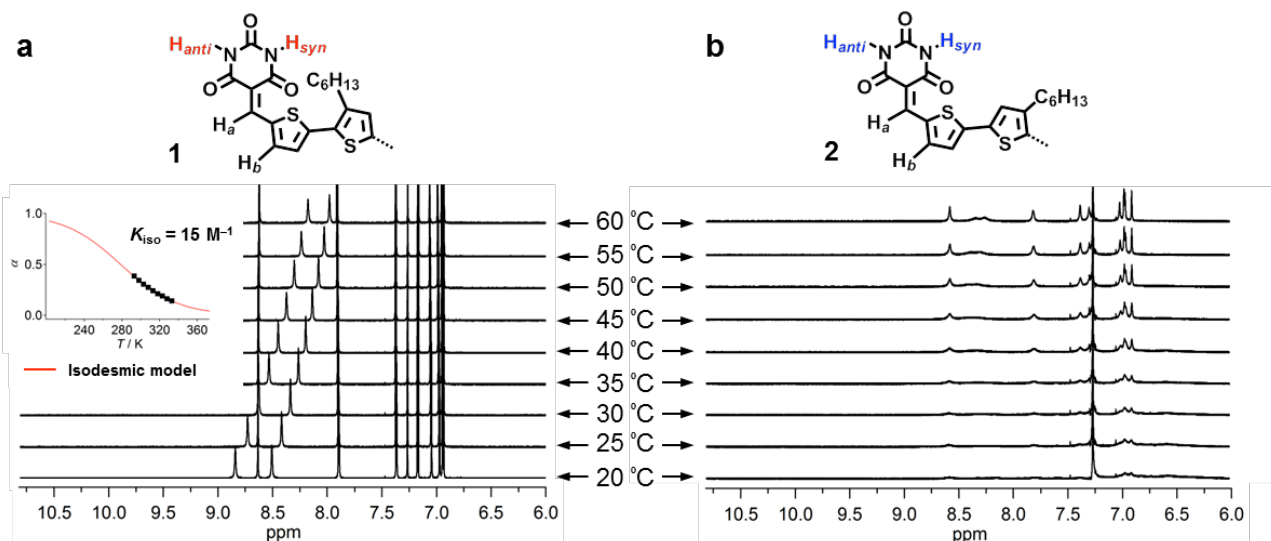


Figure S13. Temperature-dependent ^1H NMR spectra of **1** (a) and **2** (b) at $c = 20$ mM in CDCl_3 upon heating from 20 °C to 60 °C. Inset in (a): Inset: fraction of aggregated molecules (α) calculated from the chemical shift changes of the NH protons of **1** as a function of the temperature. Red solid curve represent simulated curves according to isodesmic model.

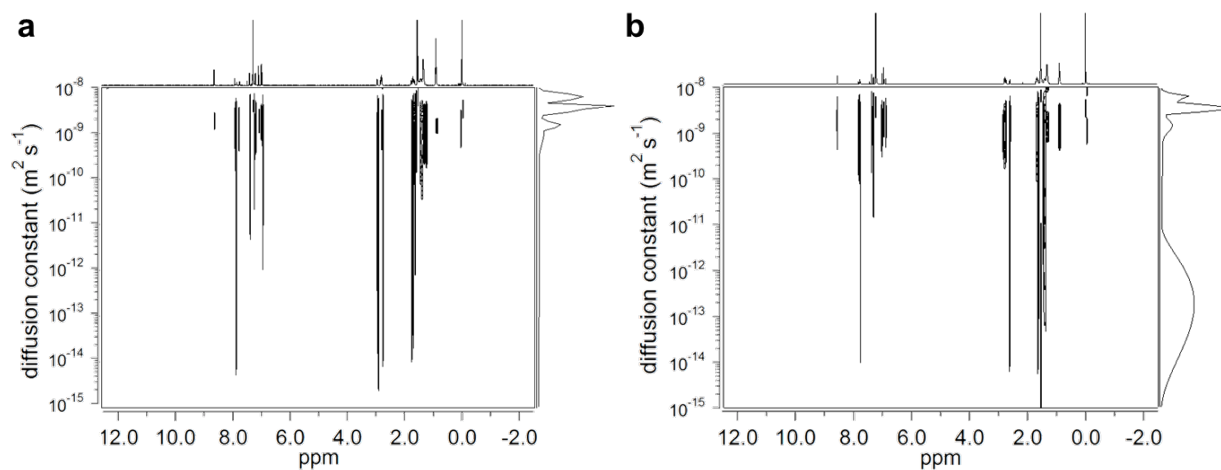


Figure S14. DOSY spectra of **1** (a) and **2** (b) in CDCl_3 at $c = 1$ mM.

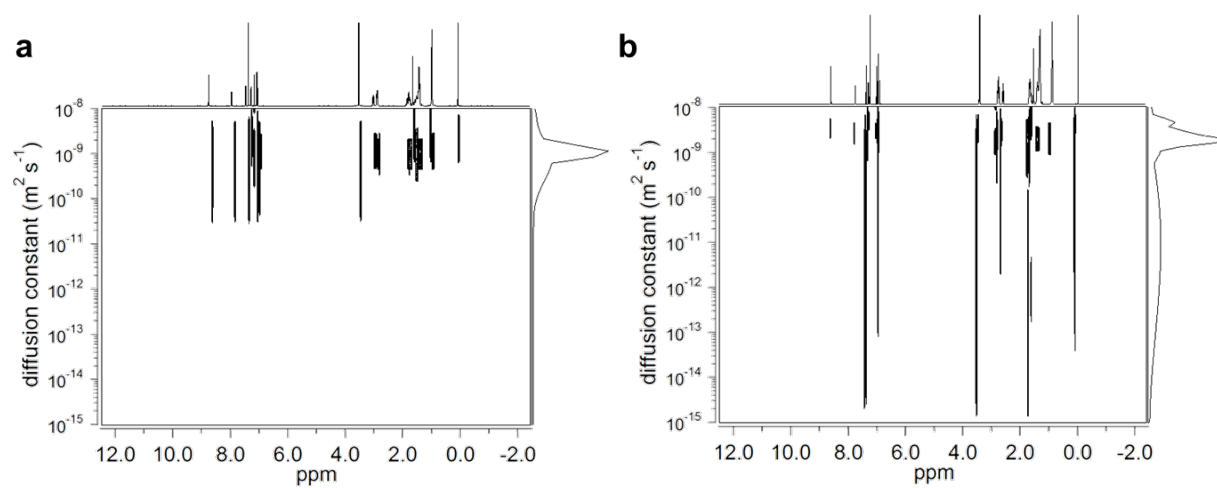


Figure S15. DOSY spectra of **1-Me** (a) and **2-Me** (b) in CDCl_3 at $c = 10 \text{ mM}$.

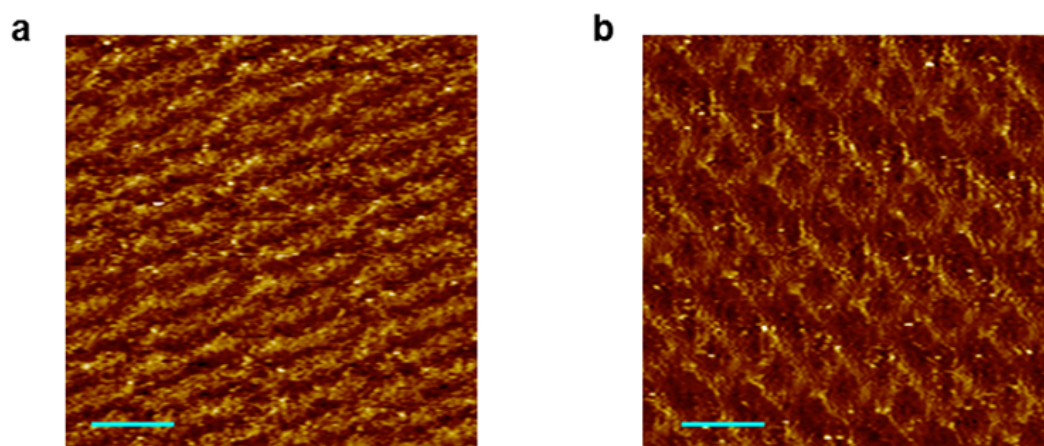


Figure S16. STM images of **1-Me** (a) and **2-Me** (b) at 1-phenyloctane–HOPG interface. The tunneling conditions: (a) $I = 3.0 \text{ pA}$, $V = -480 \text{ mV}$; (b) $I = 1.6 \text{ pA}$, $V = -600 \text{ mV}$. Scale bar, 3 nm.

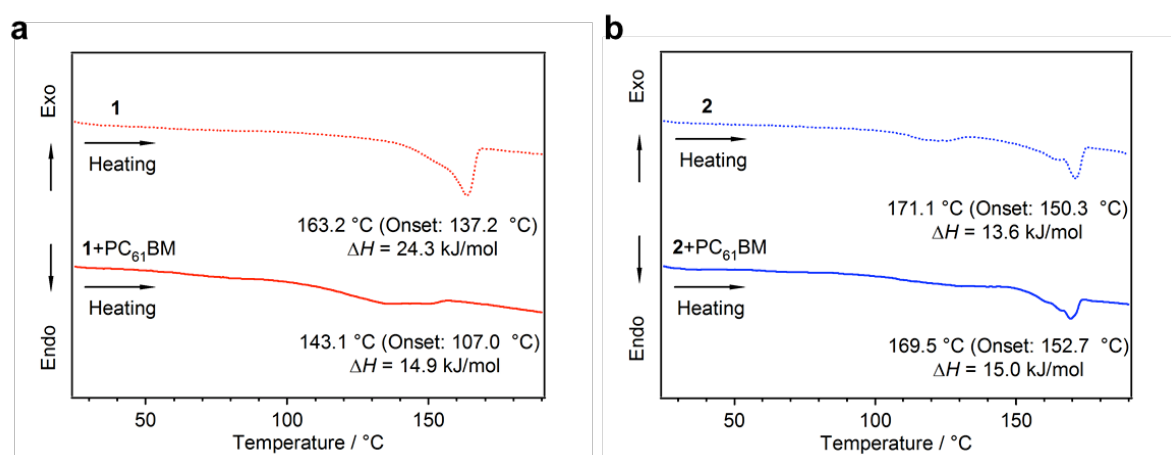


Figure S17. DSC profiles (first heating) of **1** (broken curve) and **1**:PC₆₁BM (solid curve) (**a**) and **2** (broken curve) and **2**:PC₆₁BM (solid curve) (**b**) measured at a scan rate of 5 °C/min. All samples were prepared by drop-casting CHCl₃ solutions onto a glass plate to form thin films. 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.

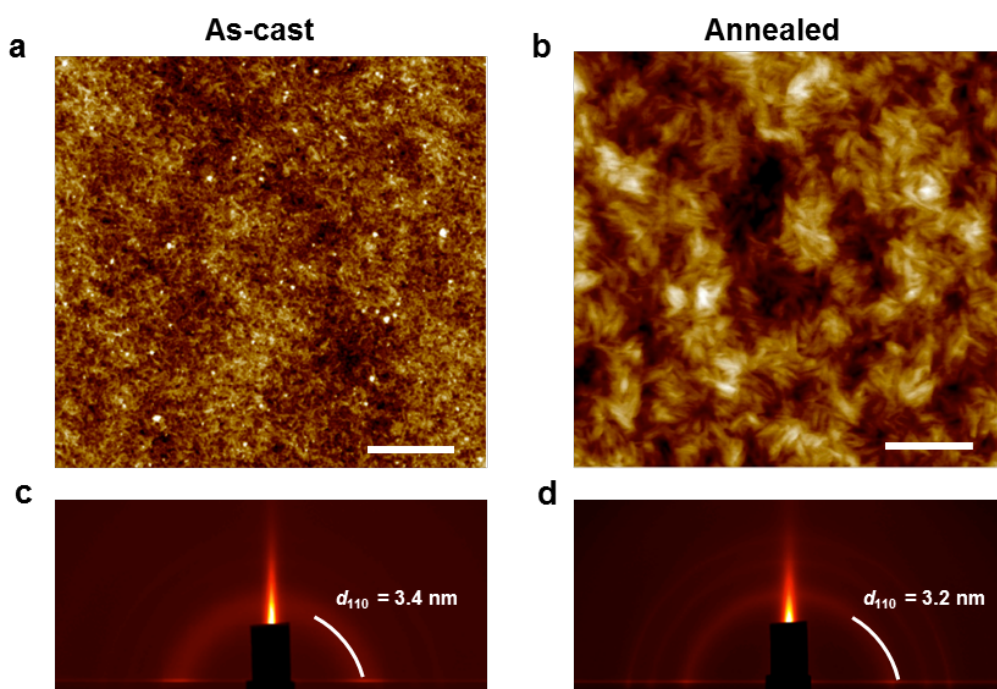


Figure S18. AFM (a,b) and GI-XRD (c,d) images of as-cast (a,c) and annealed (b,d) thin films of **1**. Scale bar, 200 nm. Thin film samples were prepared by spin-coating CHCl₃ solutions of **1** ($c = 50$ mM) onto silicon substrates. Annealing conditions: $T = 80$ °C, $t = 10$ min.

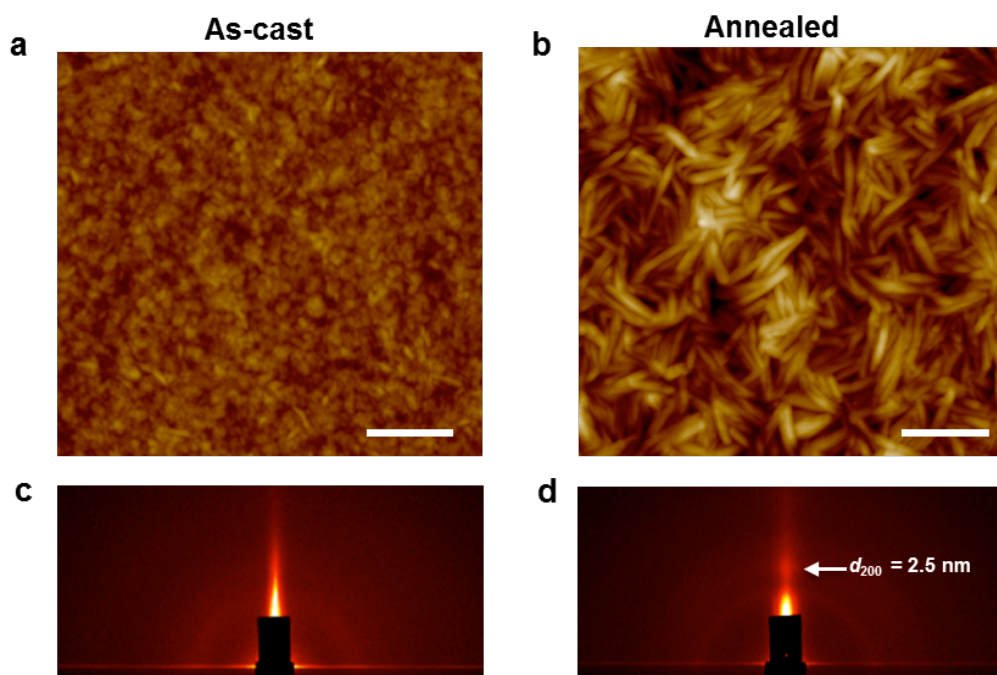


Figure S19. AFM (a,b) and GI-XRD (c,d) images of as-cast (a,c) and annealed (b,d) thin films of **1**:PC₆₁BM. Scale bar, 200 nm. Samples were prepared by spin-coating CHCl₃ solutions of the mixture ($c_{\text{total}} = 20 \text{ mg mL}^{-1}$) onto silicon substrates. Annealing conditions: $T = 80 \text{ }^{\circ}\text{C}$, $t = 10 \text{ min}$

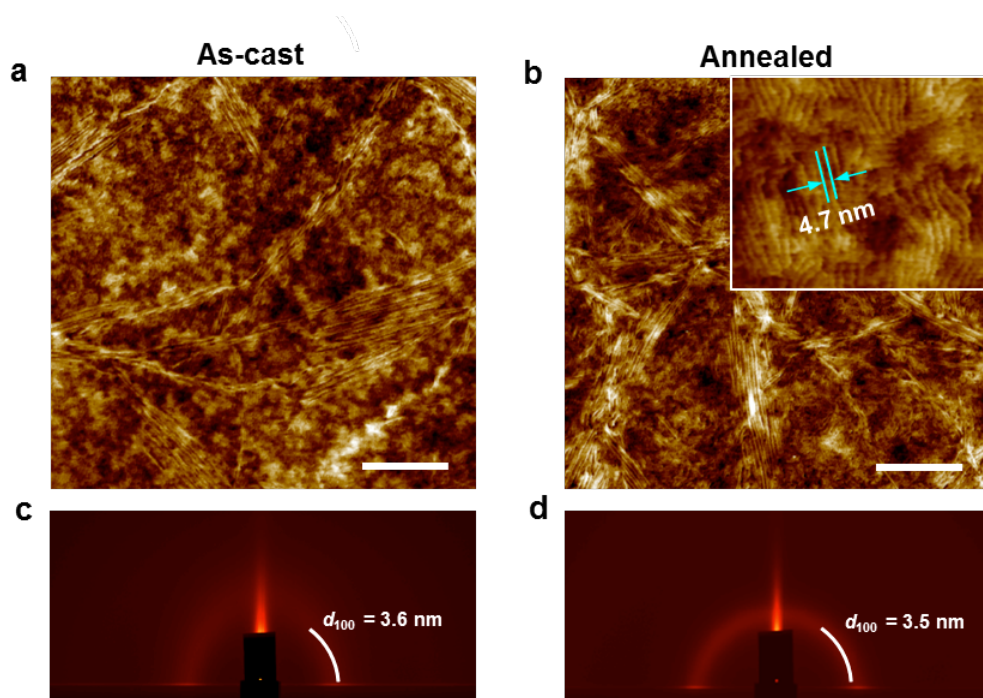


Figure S20. AFM (a,b) and GI-XRD (c,d) images of as-cast (a,c) and annealed (b,d) thin films of **2**. Scale bar, 200 nm. Thin film samples were prepared by spin-coating CHCl₃ solutions of **2** ($c = 50 \text{ mM}$) onto silicon substrates. Annealing conditions: $T = 80 \text{ }^{\circ}\text{C}$, $t = 10 \text{ min}$.

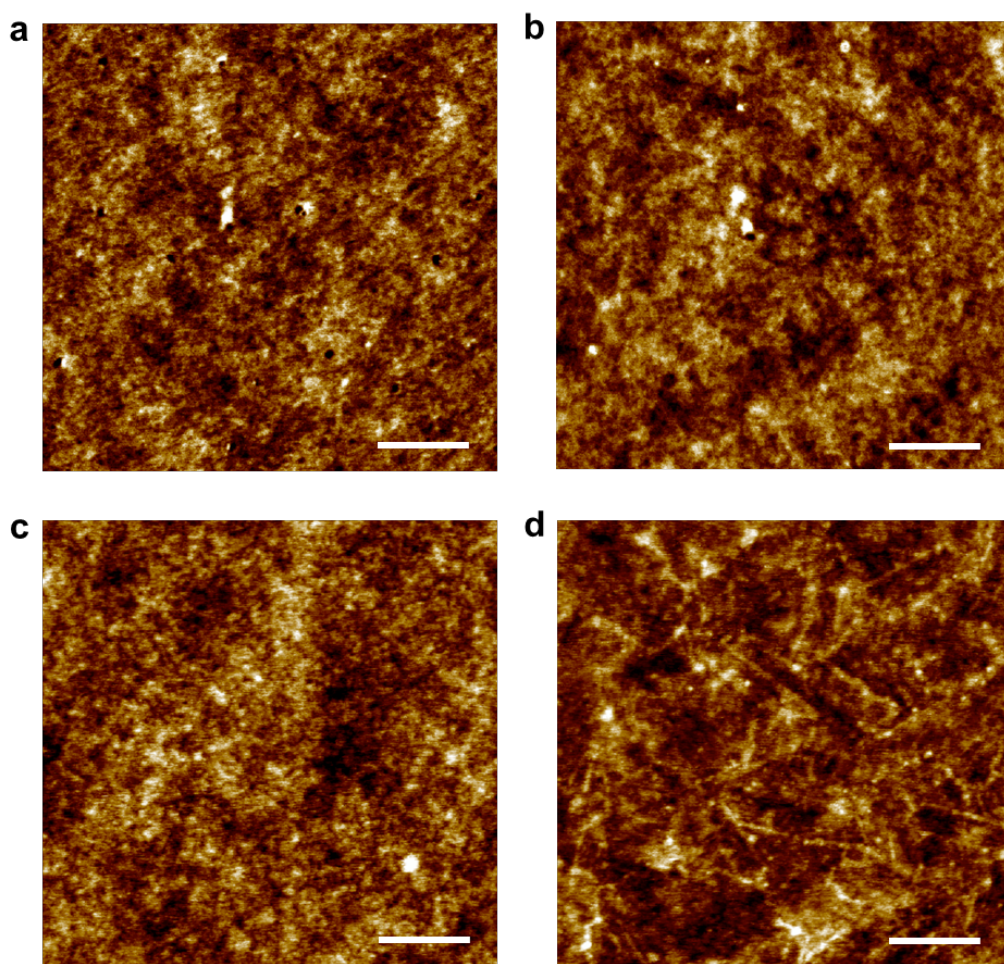


Figure S21. AFM images of 1:1 (w:w) blend films of **1-Me:PC₆₁BM** (**a,c**) and **2-Me:PC₆₁BM** (**b,d**) before (**a,b**) and after annealing at 80 °C (**c,d**). Scale bar, 200 nm.

Table S1. Comparison of the electronic properties of **1**, **2**, **1-Me**, and **2-Me**.

materials	E_g (eV)	E_{HOMO} (eV)	E_{LUMO} (eV)
1	1.84	−5.06	−3.22
2	1.78	−5.10	−3.32
1-Me	1.74	−5.11	−3.37
2-Me	1.78	−5.03	−3.25

Table S2. SCLC hole mobilities of **1** and **2**.

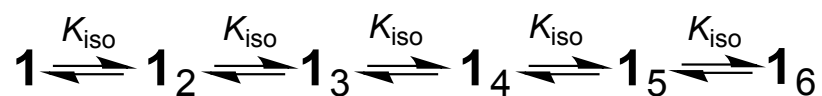
materials	annealing temp. (°C)	hole mobility ($10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$)
1	as-cast	6.5
	80	12.9
2	as-cast	17.1
	80	1.1

Table S3. Performance of BHJ solar cells of **1**:PC₆₁BM and **2**:PC₆₁BM.

BHJ films	annealing temp. (°C)	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)	PCE (%)
1 :PC ₆₁ BM	as-cast	0.88 ± 0.03	2.97 ± 0.06	28.9 ± 0.6	0.76 ± 0.04
	50	0.80 ± 0.09	2.53 ± 0.04	28.4 ± 1.1	0.58 ± 0.09
	80	0.77 ± 0.01	5.18 ± 0.00	37.8 ± 0.6	1.51 ± 0.04
	110	0.74 ± 0.03	2.67 ± 0.04	35.6 ± 0.3	0.70 ± 0.02
2 :PC ₆₁ BM	as-cast	0.85 ± 0.01	2.20 ± 0.01	41.6 ± 0.6	0.78 ± 0.02
	50	0.85 ± 0.01	2.21 ± 0.02	40.2 ± 0.3	0.75 ± 0.02
	80	0.79 ± 0.01	1.30 ± 0.03	33.2 ± 0.1	0.34 ± 0.01
	110	0.69 ± 0.01	1.74 ± 0.02	38.5 ± 0.3	0.46 ± 0.02

Table S4. Performance of BHJ solar cells of **1-Me:PC₆₁BM** and **2-Me:PC₆₁BM**.

BHJ films	annealing temp. (°C)	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF (%)	PCE (%)
1-Me:PC₆₁BM	as-cast	0.84 ± 0.06	3.75 ± 0.06	25.5 ± 0.2	0.8 ± 0.08
	50	0.63 ± 0.10	2.24 ± 0.03	25.5 ± 0.4	0.40 ± 0.09
	80	0.83 ± 0.07	4.00 ± 0.02	25.5 ± 0.3	0.85 ± 0.06
	110	0.85 ± 0.02	1.39 ± 0.01	24.6 ± 0.1	0.29 ± 0.01
2-Me:PC₆₁BM	as-cast	0.85 ± 0.01	231 ± 0.01	26.0 ± 0.2	0.51 ± 0.01
	50	0.85 ± 0.04	2.74 ± 0.04	31.3 ± 1.0	0.73 ± 0.06
	80	0.79 ± 0.01	1.84 ± 0.02	25.0 ± 0.2	0.37 ± 0.01
	110	0.76 ± 0.11	1.34 ± 0.06	24.4 ± 0.4	0.25 ± 0.05

**Scheme S1.** Formation of rosette **1₆** by isodesmic binding of **1** with K_{iso} .

Supplementary References

S1. Yagai, S. *et al.* Supramolecular engineering of oligothiophene nanorods without insulators: hierarchical association of rosettes and photovoltaic properties. *Chem. Eur. J.* **20**, 16128–16137 (2014).