

Supporting Information to:

Axisymmetric heptacyclic lactam unit for efficient polymer solar cells

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1. General characterization

^1H and ^{13}C NMR spectra were measured on a Bruker Avance-500 spectrometer. Mass spectrometry was measured on a Bruker Biflex III MALDI TOF. Elemental analyses were carried out using a FLASH EA1112 elemental analyzer. Absorption spectra were recorded on a Shimadzu UV-1800 spectrophotometer. Gel permeation chromatography (GPC) were performed on a Waters 1515-2410 series GPC coupled with differential refractive index detector. Thermogravimetric analysis was measured on a Netzsch TG 209 analyzer under a nitrogen flow at a heating rate of 10 °C/min. X-ray diffraction (XRD) of thin films was performed on a RIGAKU D/MAX-TTRIII (CBO) with Cu K α radiation. Cyclic voltammetry was conducted on a Shanghai Chenhua CHI760 voltammetric analyzer under argon in an anhydrous acetonitrile solution of tetra-n-butylammonium hexafluorophosphate (0.1 M). A glassy carbon electrode was used as the working electrode, a platinum-wire was used as the counter electrode, and a Ag/Ag $^+$ electrode was used as the reference electrode. Polymers were coated onto glassy carbon electrode and all potentials were corrected against Fc/Fc $^+$. The morphology of blended film was observed using a Digital Instruments Enviro Scope atomic force microscope (AFM) in the tapping mode.

2. Synthesis

All reagents were purchased from Alfa Aesar Co., Aladdin Co., J&K Co., InnoChem Co. and other commercial suppliers. *N*-(2-Octyldodecyl)thiophen-3-amine, $\text{TMPMgCl}\cdot\text{LiCl}$, 2,6-dichlorodithieno[3,2-*b*:2',3'-*d*]thiophene (2), ethyl 2,6-dichlorodithieno[3,2-*b*:2',3'-*d*]thiophene-3-carboxylate (3), diethyl 2,6-dichlorodithieno[3,2-*b*:2',3'-*d*]thiophene-3,5-dicarboxylate (4), and diethyl dithieno[3,2-*b*:2',3'-*d*]thiophene-3,5-dicarboxylate (5) were prepared according to literatures.^{1,2}

2,6-Dichlorodithieno[3,2-*b*:2',3'-*d*]thiophene (2). White solid (yield: 65.4%). ^1H NMR (CDCl_3 , 500 MHz, δ /ppm): 7.16 (s, 2H). ^{13}C NMR (CDCl_3 , 125 MHz, δ /ppm): 137.71, 129.97, 128.17, 119.83.

Ethyl 2,6-dichlorodithieno[3,2-*b*:2',3'-*d*]thiophene-3-carboxylate (3). White solid (yield: 48.0%). ¹H NMR (CDCl₃, 500 MHz, δ/ppm): 7.20 (s, 1H), 4.46 (q, *J* = 7.1 Hz, 2H), 1.47 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (CDCl₃, 125 MHz, δ/ppm): 160.62, 139.72, 138.77, 136.75, 130.76, 127.84, 125.11, 122.87, 119.92, 61.67, 14.22.

Diethyl 2,6-dichlorodithieno[3,2-*b*:2',3'-*d*]thiophene-3,5-dicarboxylate (4). White solid (yield: 51.8%). ¹H NMR (CDCl₃, 500 MHz, δ/ppm): 4.48 (q, *J* = 7.1 Hz, 4H), 1.49 (t, *J* = 7.1 Hz, 6H). ¹³C NMR (CDCl₃, 125 MHz, δ/ppm): 160.56, 140.63, 137.60, 124.46, 123.01, 61.72, 14.22.

Diethyl dithieno[3,2-*b*:2',3'-*d*]thiophene-3,5-dicarboxylate (5). White solid (yield: 89.8%). ¹H NMR (CDCl₃, 500 MHz, δ/ppm): 8.18 (s, 2H), 4.45 (q, *J* = 7.1 Hz, 4H), 1.47 (t, *J* = 7.1 Hz, 6H). ¹³C NMR (CDCl₃, 125MHz, δ/ppm): 161.65, 142.84, 133.13, 130.01, 127.28, 61.37, 14.32.

Diethyl 2,6-dibromodithieno[3,2-*b*:2',3'-*d*]thiophene-3,5-dicarboxylate (6). To a solution of compound **5** (0.84 g, 2.47 mmol) in CHCl₃ (50 mL) was added bromine (0.8 mL, 15.6 mmol) dropwise. The mixture was stirred at room temperature overnight and then poured into aq. Na₂SO₃ solution and extracted with CHCl₃ three times. The combined organic phase was washed with water and dried over anhydrous MgSO₄. After removal of the solvent, the crude product was purified through a silica gel column with petroleum ether/CH₂Cl₂ (1:1) to give compound **6** as a white solid (1.17 g, 95.2%). ¹H NMR (CDCl₃, 500 MHz, δ/ppm): 4.48 (q, *J* = 7.1 Hz, 4H), 1.50 (t, *J* = 7.1 Hz, 6H). ¹³C NMR (CDCl₃, 125 MHz, δ/ppm): 160.71, 141.55, 127.80, 124.96, 120.43, 61.75, 14.21.

2,6-Dibromodithieno[3,2-*b*:2',3'-*d*]thiophene-3,5-dicarboxylic acid (7). A mixture of compound **6** (1.21 g, 2.43 mmol) and sodium hydroxide (1.0 g, 25 mmol) in ethanol/THF/water (50 mL/50 mL/5 mL) was refluxed overnight. Half of solvent was evaporated under vacuum, then water (50 mL) was added to the solution. The resulting mixture was treated with HCl. The

precipitate was filtered and washed with water to give compound **7** as a pale-yellow solid (0.95 g, 88.7%). ¹³C NMR (*d*₆-DMSO, 125 MHz, δ/ppm): 162.12, 140.98, 128.26, 125.20, 121.07.

2,6-Dibromo-*N*³,*N*⁵-bis(2-octyldodecyl)-*N*³,*N*⁵-di(thiophen-3-yl)dithieno[3,2-*b*:2',3'-*d*]thiophene-3,5-dicarboxamide (8**).**

To a solution of compound **7** (0.95 g, 2.13 mmol) in dry CH₂Cl₂ (40 mL) were added oxalyl chloride (2 mL, 23.5 mmol) and 2 drops of DMF. The mixture was stirred at room temperature overnight. The solvent was removed under vacuum to obtain 2,6-dibromodithieno[3,2-*b*:2',3'-*d*]thiophene-3,5-dicarbonyl dichloride, which was used in next step without purification. To the solution of 2,6-dibromodithieno[3,2-*b*:2',3'-*d*]thiophene-3,5-dicarbonyl dichloride in dry CH₂Cl₂ (30 mL) was slowly added a solution of *N*-(2-octyldodecyl)thiophen-3-amine (2.2 g, 5.79 mmol) and Et₃N (2 mL) in dry CH₂Cl₂ (30 mL) at 0 °C. The mixture was stirred at room temperature overnight. Then the mixture was poured into water and extracted with CHCl₃ three times. The organic phase was dried over anhydrous MgSO₄. After removal of the solvent, the crude product was purified through a silica gel column with petroleum ether/CH₂Cl₂ (1:2) to give compound **8** as a deep yellow solid (1.42 g, 57.3%). ¹H NMR (CDCl₃, 500 MHz, δ/ppm): 7.05 (br, 2H), 6.95 (s, 2H), 6.81 (br, 2H), 3.84 (br, 4H), 1.65 (br, 2H), 1.37-1.26 (m, 64H), 0.89-0.87 (m, 12H). ¹³C NMR (CDCl₃, 125 MHz, δ/ppm): 163.50, 139.22, 137.63, 132.34, 129.20, 125.08, 119.60, 111.21, 52.69, 36.13, 31.90, 31.07, 30.07, 29.65, 29.60, 29.34, 26.23, 22.67, 14.12.

TD3. To a solution of compound **8** (1.07 g, 0.092 mmol) in *N,N*-dimethylacetamide (80 mL) were added PCy₃·HBF₄ (300 mg, 0.82 mmol), Cs₂CO₃ (2.5 g, 7.7 mmol) and Pd(OAc)₂ (150 mg, 0.65 mmol) under Ar. The mixture was stirred at 115 °C for 20 h and then cooled to room temperature. The mixture was poured into water and extracted with CHCl₃ three times. The combined organic phase was washed with brine and dried over anhydrous MgSO₄. The solvent was removed under reduced pressure and the residue was purified through a silica gel column with petroleum ether/CH₂Cl₂ (1:1) as eluent to give **TD3** as a yellow solid (0.47 g, 51.1%). ¹H NMR (CDCl₃, 500 MHz, δ/ppm): 7.46 (d, *J* = 5.1 Hz, 2H), 7.10 (d, *J* = 5.3 Hz, 2H), 4.28 (br, 4H), 2.05 (br, 2H), 1.38-1.21(m, 64H), 0.88-0.85 (m, 12H). ¹³C NMR (CDCl₃, 125 MHz,

δ /ppm): 157.39, 142.28, 141.70, 140.96, 125.86, 125.55, 122.35, 117.59, 114.69, 49.16, 37.23, 31.90, 31.86, 31.49, 29.97, 29.68, 29.61, 29.56, 29.51, 29.33, 29.27, 26.57, 22.66, 22.65, 14.10. MALDI-TOF MS (m/z): 1003.499 (M^+). Elemental analysis (%) calcd for $C_{58}H_{86}N_2O_2S_5$: C, 69.41; H, 8.64; N, 2.79. Found: C, 69.34; H, 8.60, N, 2.52.

TD3-Br. To a solution of **TD3** (400 mg, 0.40 mmol) in a mixed solvent of $CHCl_3$ (30 mL) and DMF (15 mL) was added NBS (156 mg, 0.88 mmol) under Ar. The mixture was stirred at room temperature for 24 h and then poured into water and extracted with $CHCl_3$ three times. The combined organic phase was washed with brine and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure and the crude product was purified by chromatography over silica gel using petroleum ether/ CH_2Cl_2 (1:1) as eluent to give compound **TD3-Br** as a yellow solid (354 mg, 76.5%). 1H NMR ($CDCl_3$, 500 MHz, δ /ppm): 6.98 (s, 2H), 4.17 (br, 4H), 1.94 (br, 2H), 1.37-1.21 (m, 64H), 0.86-0.83 (m, 12H). ^{13}C NMR ($CDCl_3$, 125 MHz, δ /ppm): 156.63, 141.43, 140.76, 139.64, 125.51, 121.93, 120.39, 115.33, 114.48, 49.11, 37.15, 31.89, 31.87, 31.35, 29.97, 29.62, 29.58, 29.53, 29.33, 29.29, 26.46, 22.66, 14.11. MALDI-TOF MS (m/z): 1160.178 (M^+). Elemental analysis (%) calcd for $C_{58}H_{84}Br_2N_2O_2S_5$: C, 59.98; H, 7.29, N, 2.41. Found: C, 60.08; H, 7.26, N, 2.41.

PThTD3. **TD3-Br** (120 mg, 0.10 mmol) and 2,5-bis(trimethylstannyl)thiophene (42 mg, 0.10 mmol) were dissolved in 30 mL toluene, and the solution was flushed with argon for 15 min, then 12 mg $Pd(PPh_3)_4$ was added into the solution. The mixture was flushed again with argon for 20 min. The reaction solution was heated to reflux for 24 h. Then the solution was cooled to room temperature and added dropwise to 150 mL methanol. The precipitate was collected and further purified by Soxhlet extraction with methanol, hexane, and chloroform in sequence. The chloroform fraction was concentrated and added dropwise into methanol. Subsequently, the precipitate was collected and dried under vacuum overnight to give **PThTD3** as a black solid (94 mg, 83.9%). Elemental analysis (%) calcd for $C_{62}H_{86}N_2O_2S_6$: C, 68.71; H, 8.00; N, 2.58. Found: C, 68.57; H, 7.86, N, 2.52.

3. NMR spectra

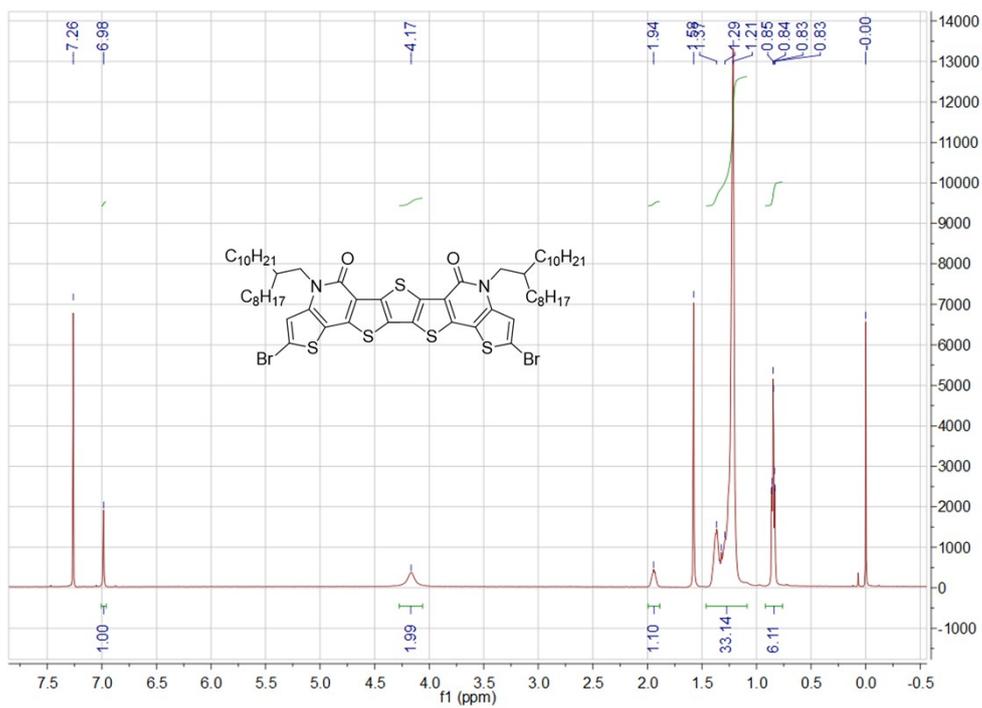


Fig. S1 ¹H NMR spectrum of TD3-Br.

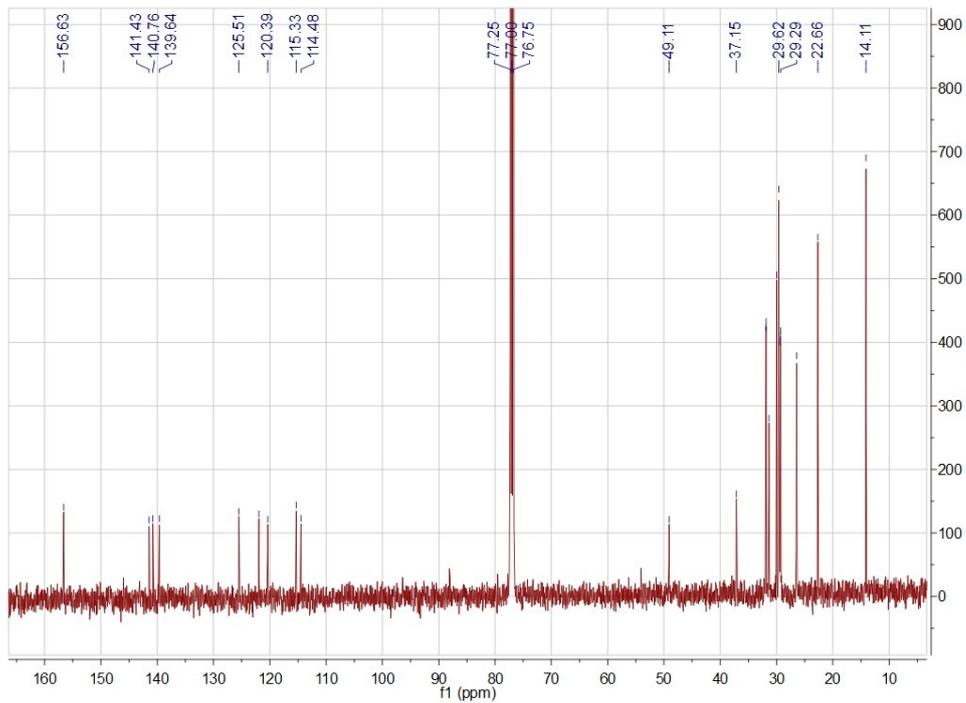


Fig. S2 ¹³C NMR spectrum of TD3-Br.

4. TGA

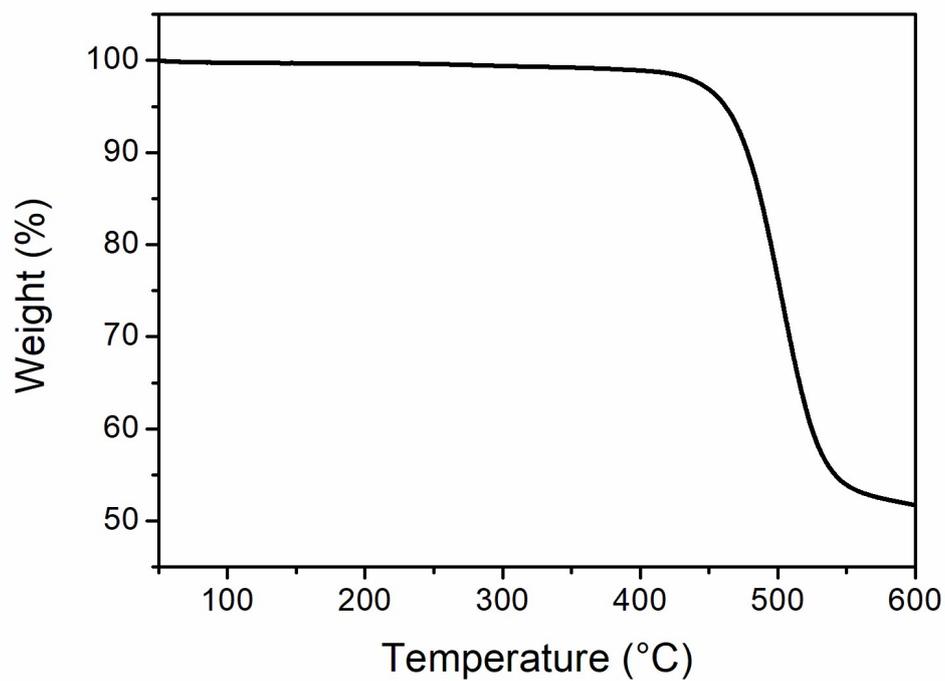


Fig. S3 TGA curve for PThTD3.

5. CV

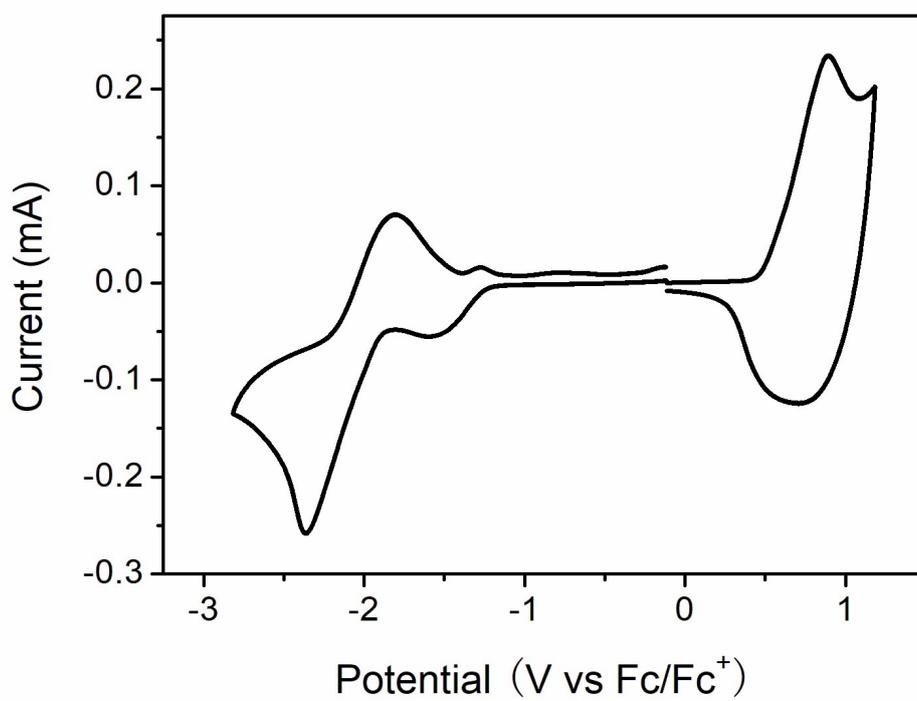


Fig. S4 Cyclic voltammogram for PThTD3.

6. Device fabrication and measurements

Inverted solar cells

Inverted solar cells were fabricated on ITO-coated glass substrates. The ITO-coated glass substrates were first cleaned with detergent, and then ultrasonicated in water, acetone and isopropyl alcohol, and subsequently dried with a flowing nitrogen stream. The ZnO precursor was prepared by dissolving zinc acetate dihydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, 1 g) and ethanolamine ($\text{NH}_2\text{CH}_2\text{CH}_2\text{OH}$, 0.28 g) in 2-methoxyethanol ($\text{CH}_3\text{OCH}_2\text{CH}_2\text{OH}$, 10 mL) under vigorous stirring for 12 h for the hydrolysis reaction in air. The ZnO precursor solution was spin-cast on top of the ITO-glass substrate. The films were annealed at 200 °C for 1 h in air. The ZnO films thickness were approximately 30 nm and were transferred into a glove box. A PThTD3:PC₇₁BM blend in chlorobenzene with DIO additive (0~3 vol%) was spin-coated onto ZnO layer. Finally, MoO₃ (6 nm) and Al (100 nm) were thermally evaporated under a shadow mask (pressure ca. 10⁻⁴ Pa). The effective area for the devices is 4 mm². The current density voltage (*J-V*) characteristics for the devices were measured in a glovebox using a Keithley 2400 source meter and an Air Mass 1.5 Global solar simulator (Taiwan, Enlitech). The irradiation intensity of the light source was calibrated by a standard silicon solar cell with a KG5 filter, modulated a value of 100 mW cm⁻². EQE values were tested with a commercial EQE measurement system (Taiwan, Enlitech, QE-R) during illumination with chopped monochromatic light from a xenon lamp. The film thickness was measured using a surface profiler (XP-100).

Hole-only devices

The structure for hole-only devices is ITO/PEDOT:PSS/active layer/MoO₃/Al. A 30 nm thick PEDOT:PSS layer was formed on ITO substrates by spin coating an aqueous dispersion onto ITO glass (3500 rpm for 30 s). PEDOT:PSS coated substrates were dried at 150 °C for 10 min. A PThTD3:PC₇₁BM (1:1.5) blend in chlorobenzene with 2 vol% DIO additive was spin-coated onto PEDOT:PSS layer. Finally, MoO₃ (6 nm) and Al (100 nm) were successively evaporated onto the active layer under a shadow mask (pressure ca. 10⁻⁴ Pa). *J-V* curves were measured with a computerized Keithley 2400 SourceMeter in the dark.

7. Optimization of device performance

Table S1 Optimization of D/A ratio for PThTD3:PC₇₁BM inverted solar cells.^a

D/A	V_{oc}	J_{sc}	FF	PCE
[w/w]	[V]	[mA/cm ²]	[%]	[%]
1:1.0	0.84	12.54	66.15	6.97 (6.68)
1:1.5	0.84	12.87	67.05	7.25 (6.94)
1:2.0	0.84	12.35	65.49	6.79 (6.47)

^a Blend solution: 12 mg/mL in CHCl₃ with 2 vol% DIO; spin coating: 2000 rpm for 30 s.

Table S2 Optimization of the active layer thickness for PThTD3:PC₇₁BM inverted solar cells.^a

Thickness	V_{oc}	J_{sc}	FF	PCE
[nm]	[V]	[mA/cm ²]	[%]	[%]
100	0.84	12.87	67.05	7.25 (6.94)
140	0.83	12.43	59.35	6.12 (5.83)
170	0.82	12.02	54.35	5.36 (5.04)

^a D/A ratio: 1:1.5 (w/w); blend solution: 12 mg/mL in CHCl₃ with 2 vol% DIO.

8. AFM

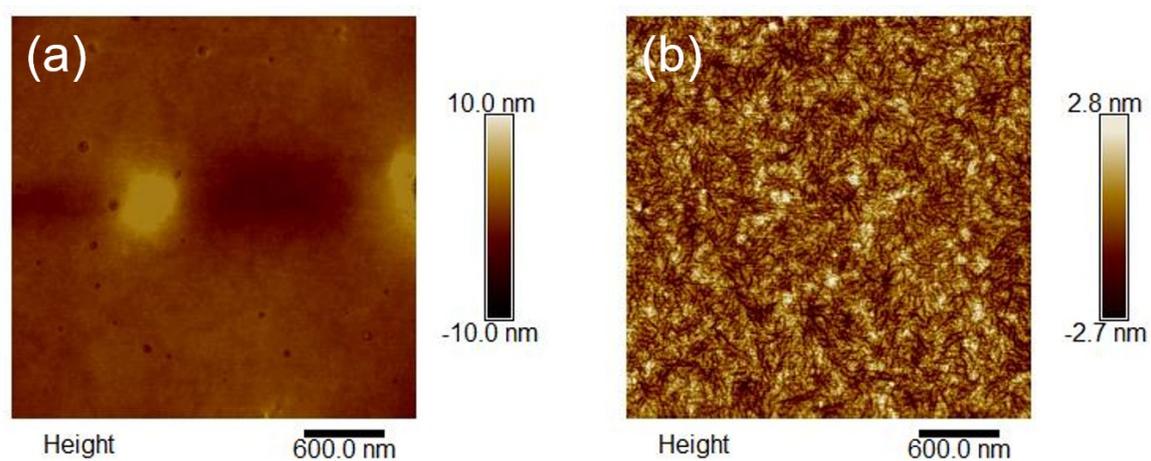


Fig. S5 AFM height images of PThTD3:PC₇₁BM blend films without (a) or with 2% DIO (b).

References

- [1] R. S. Ashraf, A. J. Kronemeijer, D. I. James, H. Sirringhaus and I. McCulloch, *Chem. Commun.*, 2012, **48**, 3939.
- [2] T. Kunz and P. Knochel, *Chem. Eur. J.*, 2011, **17**, 866.