

ASSOCIATED CONTENT

Supporting Information

Evolution of Polymer Photovoltaic Performances from Subtle Chemical Structure Variations

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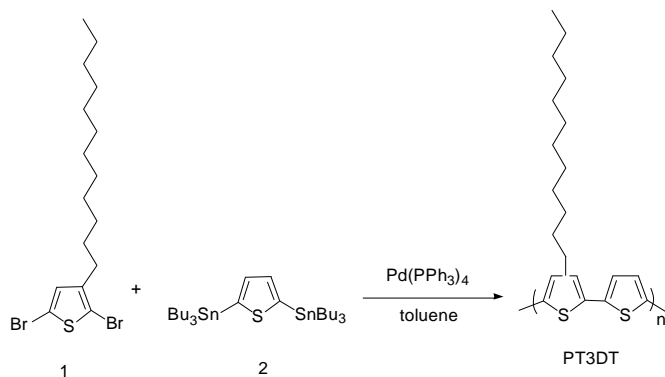
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The synthesis process of P3DDTT, microscopy and AFM height images are listed in this part. Also the device performance details are involved. This material is available free of charge via the Internet at <http://pubs.acs.org>.

1. Synthesis and characterization of P3DDTT



2,5-dibromo-3-dodecylthiophene (1). This compound was synthesized by a literature procedure.¹ Yield: 85%. ¹H NMR (CDCl₃, 400 MHz): δ (ppm) 7.01 (s, 1H, Ar H), 2.60 (t, 2H, Ar-CH₂), 1.62 (m, 2H, CH₂), 1.30 (m, 18H, CH₂), 1.95 (t, 3H, CH₃). MS: *m/z* = 408.

2,5-Bis(tributylstannyl)thiophene (2). Thiophene (8.4 g, 0.10 mol) was dissolved in 60 ml THF in a well-dried flask under the protection of nitrogen. *n*-Butyl lithium (88 ml, 0.22 mol, 2.5

mol/L in hexane) was added dropwise, and the solution was stirred under reflux for 2 hours. After being cooled down to ambient temperature, tributylchlorostannane (70 g, 0.21 mol) was added in one portion. After 12 hours, the solution was poured into 100 ml cool water. The organic layer was separated, and the aqua layer was extracted by ether. The organic layers were collected and dried over anhydrous MgSO₄, the removal of solvent gave a crude product. After distillation under vacuum (0.1 mmHg/220 °C), 32.5 g (0.049 mol) of 2,5-Bis(tributylstannyl)thiophene was obtained. Yield: 53%. ¹H NMR (CDCl₃, 400 MHz): δ (ppm) 7.34 (s, 2H, Ar H), 1.60 (M, 12H, CH₂), 1.39 (m, 12H, CH₂), 1.09 (m, 12H, CH₂), 0.91 (t, 18H, CH₃). MS (MALDI): *m/z* = 664.

Polymerization (P3DDTT), Pd(PPh₃)₄ (50 mg, 0.043 mmol), Compound **1** (1 mmol) and 2,5-Bis(tributylstannyl)thiophene (Compound **2**, 0.67 g, 1.0 mmol) were put into a three-neck flask. The mixture was flushed with argon for 10 min and then 10 ml toluene was added. At the protection of argon, the reactant was heated to reflux for 12 h. The mixture was cooled to room temperature and a solution of KF (5 g) in water (10 ml) was added and stirred at room temperature for 2 h to remove the tin impurity. The mixture was extracted with toluene (2 × 150 ml), washed with water (2 × 150 ml), and dried over anhydrous MgSO₄. The solution was concentrated to 5 ml and poured into 30 ml of methanol and then filtered into a Soxhlet thimble. Soxhlet extraction was performed with methanol, hexane, and CHCl₃. The polymer was recovered from the CHCl₃ fraction by rotary evaporation. Finally, the polymer was further purified by size exclusion column chromatography over Bio-Rad Bio-Beads S=X1 eluting with THF to afford a dark-red solid. The solid was dried under vacuum overnight. Yield: 49.8%. ¹H NMR (CDCl₃, 400 MHz): δ (ppm) 7.01-7.05 (br, 3H, Ar H), 2.77 (br, 2H, Ar-CH₂), 1.54-1.68 (br, 2H, CH₂), 1.26-1.40 (br, 18H, CH₂), 0.85 (br, 3H, CH₃).

[1] Hou, J.; Yang, C.; Qiao, J.; Li, Y. *Synth. Met.* **2005**, *150*, 297.

[2] You, W.; Yang, Y.; Yeh, J. *Chem. Mater.* **1996**, *8*, 2659.

P3HT:PCBM	Voc [V]	Jsc [mA/cm ²]	FF [%]	PCE [%]
Pristine	0.62	3.92	51.07	1.37
70 °C / 10min	0.57	7.66	40.74	1.88
70 °C / 30min	0.59	7.34	49.53	2.26
70 °C / 60min	0.59	8.73	52.18	2.85
110 °C / 10min	0.58	8.54	53.44	2.83
110 °C / 30min	0.59	10.22	53.43	3.42
110 °C / 60min	0.59	10.30	58.30	3.74
150 °C / 10min	0.61	9.78	53.62	3.38
150 °C / 30min	0.61	11.38	59.82	4.43
150 °C / 60min	0.61	11.06	58.27	4.18

Table S1. The device performance of P3HT/PCBM (1:1 by weight ratio) under different annealing conditions.

P3DDT:PCBM	Voc [V]	Jsc [mA/cm²]	FF [%]	PCE [%]
Pristine	0.57	2.97	38.37	0.73
70 °C / 10min	0.55	4.88	37.26	1.12
70 °C / 30min	0.56	6.35	37.66	1.51
70 °C / 60min	0.57	7.44	38.10	1.80
110 °C / 10min	/	/	/	/
110 °C / 30min	/	/	/	/
110 °C / 60min	/	/	/	/
150 °C / 10min	/	/	/	/
150 °C / 30min	/	/	/	/
150 °C / 60min	/	/	/	/

Table S2. The device performance of P3DDT/PCBM (1:1 by weight ratio) under different annealing conditions.

P3DDTT:PCBM	Voc [V]	Jsc [mA/cm²]	FF [%]	PCE [%]
Pristine	0.61	1.25	27.97	0.24
70 °C / 10min	0.63	1.34	27.31	0.26
70 °C / 30min	0.67	1.28	28.20	0.27
70 °C / 60min	0.66	1.50	30.66	0.34
110 °C / 10min	0.67	1.45	30.54	0.33
110 °C / 30min	0.66	1.55	31.72	0.37
110 °C / 60min	0.68	1.83	28.86	0.40
150 °C / 10min	0.67	1.54	31.08	0.36
150 °C / 30min	0.69	2.68	27.93	0.58
150 °C / 60min	0.70	3.20	28.48	0.72

Table S3. The device performance of P3DDTT/PCBM (1:1 by weight ratio) under different annealing conditions.

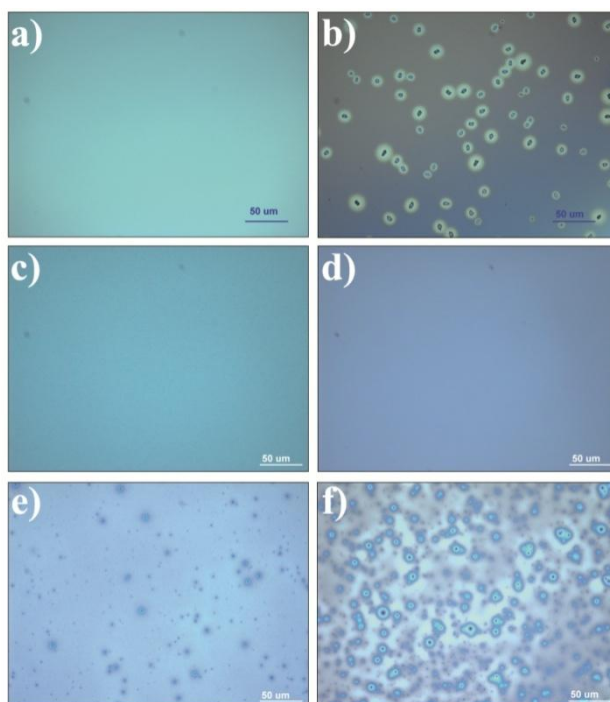


Figure S1. Microscope images of polymer/PCBM (1:1 by weight ratio) films spin-coated from ODCB. a) P3HT/PCBM blend film as cast. b) P3HT/PCBM blend film annealed at 150 °C for 30min. c) P3DDT/PCBM blend film as cast. d) P3DDT/PCBM blend film annealed at 70 °C for 1h. e) P3DDTT/PCBM blend film as cast. f) P3DDTT/PCBM blend film annealed at 150 °C for 1h.

Optical microscopy (OM) was used to investigate morphological alteration of the blends. Agglomerations are observed in P3HT blend film underwent heat treatment at 150 °C for 30min while untreated film is featureless at the micrometer scale. The agglomerations are assigned to PCBM-rich domains as previously reported. The growth process is ascribed to Ostwald ripening. The colored “halo” around the agglomerations is due to light interference originating from changes in film thickness and is attributed to PCBM-depleted regions. In contrast, the morphology of the P3DDT blend remains almost unchanged, before and after thermal annealing.

Our group has reported that the agglomeration of PCBM promoted polymer crystallization and connection with the adjacent, thus facilitated formation of the interpenetrating networks. Conversely micrometer scale agglomerations appear even without heat treatment for P3DDTT films. As we all know, dichlorobenzene dissolve PCBM well, we attribute these agglomerations to P3DDTT. After thermal annealing at 150 °C for 30min, the agglomerations grew bigger, but do not form the needle-shaped crystals. And the film appeared un-uniform all over the observed field in a large extent.

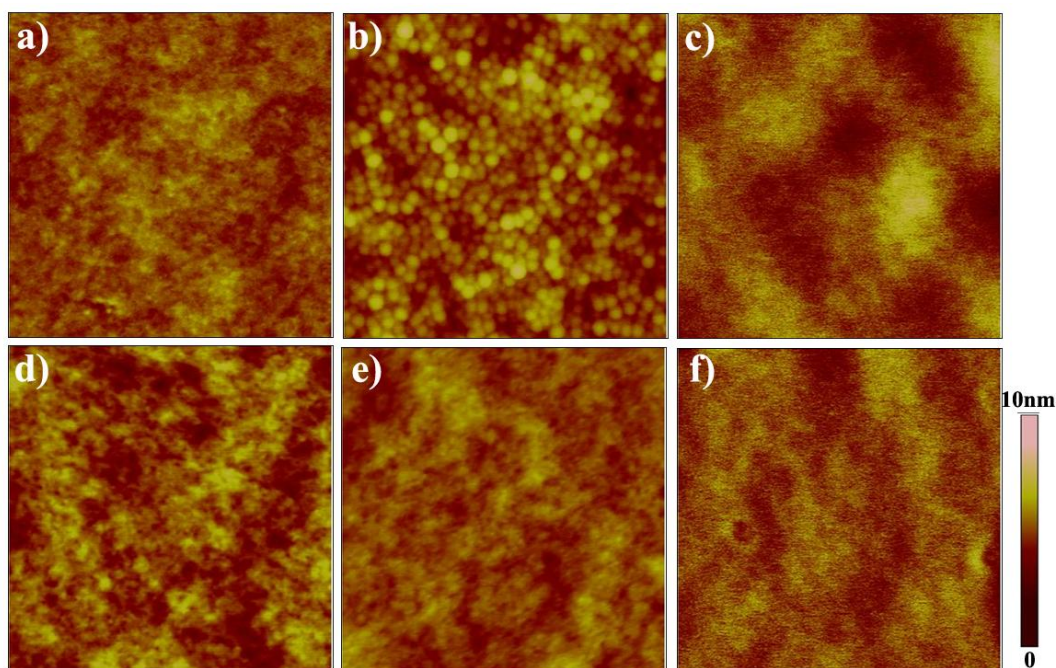


Figure S2. Tapping-mode AFM ($2\ \mu\text{m} \times 2\ \mu\text{m}$) height images with various Polymer/PCBM blend films (1:1 by weight ratio): a) P3HT/PCBM blend film as cast. b) P3DDT/PCBM blend film as cast. c) P3DDTT/PCBM blend film as cast. d) P3HT/PCBM blend film annealed at 150 °C for 30min. e) P3DDT/PCBM blend film annealed at 70 °C for 1h. f) P3DDTT/PCBM blend film annealed at 150 °C for 1h.

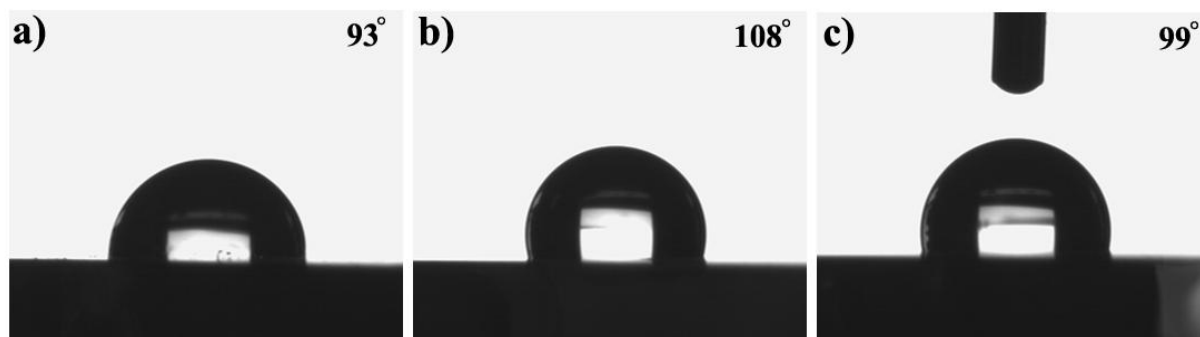


Figure S3. Contact angle of P3HT (a), P3DDT (b) and P3DDTT(c) films.