

Supporting Information

High-Performance Conjugated Terpolymer-Based Organic Bulk Heterojunction Solar Cells

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Synthesis of polymers

2,5-bis(3-ethyl-hexy-thiophen-2yl)-thieno[3,2-b]thiophene (3a)

2a (2.33 g, 5 mmol) and 2-bromo-3-(2-ethylhexyl)-thiophene, (2.76 g, 10 mmol) were dissolved into 40 ml toluene in a flask protected by nitrogen. The solution was flushed with nitrogen for 10 min and then 300 mg of Pd(PPh₃)₄ was added into the flask. The reaction mixture was stirred for 24 h at 110°C under nitrogen atmosphere. Then the solvent was evaporated and the residue was purified by silica gel column chromatography (Petroleum ether) to afford yellow oil. (2.41 g, 91% yield). ¹H NMR (CDCl₃, 300 MHz, ppm): δ 7.12 (s, 2H), 7.07 (d, 2H), 6.81 (d, 2H), 2.63 (d, 4H), 1.55 (m, 2H), 1.23-1.22 (m, 16H), 0.76-0.71 (m, 12H). ¹³C NMR (CDCl₃, 600 MHz): d (ppm) 138.4, 136.6, 130.2, 129.4, 123.2, 117.3, 39.4, 32.4, 31.6, 27.7, 24.8, 22.0, 13.1, 9.8.

2,5-bis(3-ethyl-hexy-5-(trimethylstannyl)thiophen-2yl)-thieno[3,2-b]thiophene (4a)

To a solution of **3a** (1.05 g, 2 mmol) in 60 mL THF, 2M solution of LDA in hexane (2.5 mL, 5 mmol) was added dropwise at -78°C. The solution was stirred at -78 °C for 2 h and 1.0 M solution of trimethyltin chloride (6 mL, 6 mmol) in THF was added in one portion. The solution was warmed to room temperature and 50 mL of water and 50 mL of ethyl acetate were added. The organic layer was washed twice with 50 mL of water and dried over anhydrous Na₂SO₄. The organic layer was evaporated and dried over vacuum to afford a yellow oil. (1.42 g, 83% yield). ¹H NMR (CDCl₃, 300 MHz, ppm): δ 7.13 (s, 2H), 6.9 (s, 2H), 2.66 (d, 4H), 1.60 (m, 2H), 1.47-1.58 (m, 16H), 0.79-0.42 (m, 12H), 0.33 (s, 18H). ¹³C NMR (CDCl₃, 600 MHz): d (ppm) 140.5, 139.2, 138.8, 137.8, 137.0, 136.9, 117.8, 40.4, 33.3, 32.6, 28.7, 25.9, 23.1, 14.1, 10.9, 8.2.

2,5-bis(3-ethyl-hexy-thiophen-2yl)-thiazolo[5,4-d]thiazole (3b)

A solution of 3-(2-ethylhexyl)-2-thiophenecarboxaldehyde (12.34 g, 55 mmol) and dithiooxamide (3.00 g, 25.0 mmol) in N,N-dimethylformamide (50 mL) was heated under reflux for 3 h, and then cooled down to room temperature. The reaction mixture was poured

into water (100 mL) and extracted with methylene chloride. The organic layer was washed three times with water and dried over magnesium sulfate. The solvent was evaporated and the residue was purified by column chromatography on silica gel with methylene chloride. Yield: 4.11 g (31%); ^1H NMR (CDCl_3 , 300 MHz, ppm): δ 6.99 (s, 2H), 2.93 (d, 4H), 1.79-1.75 (m, 2H), 1.40-1.27 (m, 16H), 0.92-0.87 (m, 12H), 0.41 (s, 18H). ^{13}C NMR (CDCl_3 , 600 MHz): d (ppm) 161.7, 150.0, 142.4, 132.3, 131.6, 127.0, 33.9, 34.4, 32.6, 28.7, 25.8, 23.1, 14.1, 10.7.

2,5-bis(3-ethyl-hexy-5-(trimethylstannyl)thiophen-2yl)-thiazolo[5,4-d] thiazole (4b) :

To a solution of **3b** (1.06 g, 2 mmol) in 60 mL THF, 2M solution of LDA in hexane (2.5 mL, 5 mmol) was added dropwise at -78°C . The solution was stirred at -78°C for 2 h and 1.0 M solution of trimethyltin chloride (6 mL, 6 mmol) in THF was added in one portion. The solution was warmed to room temperature and 50 mL of water and 50 mL of ethyl acetate were added. The organic layer was washed twice with 50 mL of water and dried over anhydrous Na_2SO_4 . The organic layer was evaporated and dried over vacuum and residue was recrystallized by ethyl alcohol to afford a yellow solid. (1.07 g, 63% yield). ^1H NMR (CDCl_3 , 300 MHz, ppm): δ 7.34 (d, 2H), 6.95 (d, 2H), 2.92 (d, 4H), 1.79-1.75 (m, 2H), 1.40-1.27 (m, 16H), 0.94-0.85 (m, 12H). ^{13}C NMR (CDCl_3 , 600 MHz): d (ppm) 161.6, 151.2, 143.2, 139.6, 133.4, 127.8, 40.0, 34.2, 32.6, 28.6, 25.9, 23.1, 14.1, 10.7, -8.3.

Polymerization for PtDDA

Compound **4a** (171 mg, 0.2 mmol) and **T1** (153 mg, 0.2 mmol) were dissolved into 9 mL of toluene in a flask protected by nitrogen. The solution was flushed with nitrogen for 10 min and then 15 mg of $\text{Pd}(\text{PPh}_3)_4$ was added into the flask. The solution was flushed with nitrogen again for 25 min. The oil bath was heated to 110°C gradually and the reaction mixture was stirred for 11 h at 110°C under nitrogen atmosphere. Then, the mixture was cooled to room temperature, and the polymer was precipitated by the addition of 100 mL of methanol and filtered. The crude was purified by column chromatography using chloroform as eluent to obtain pure product: $M_w = 67.4$ k, $\text{PDI} = 4.2$.

Polymerization for PtDAA

Compound **4b** (172 mg, 0.2 mmol) and **T1** (153 mg, 0.2 mmol) were dissolved into 9 mL of toluene in a flask protected by nitrogen. The solution was flushed with nitrogen for 10 min and then 15 mg of Pd(PPh₃)₄ was added into the flask. The solution was flushed with nitrogen again for 25 min. The oil bath was heated to 110°C gradually and the reaction mixture was stirred for 6 h at 110°C under nitrogen atmosphere. Then, the mixture was cooled to room temperature, and the polymer was precipitated by the addition of 100 mL of methanol and filtered. The crude was purified by column chromatography using chloroform as eluent to obtain pure product: $M_w = 34.5$ k, $PDI = 3.1$.

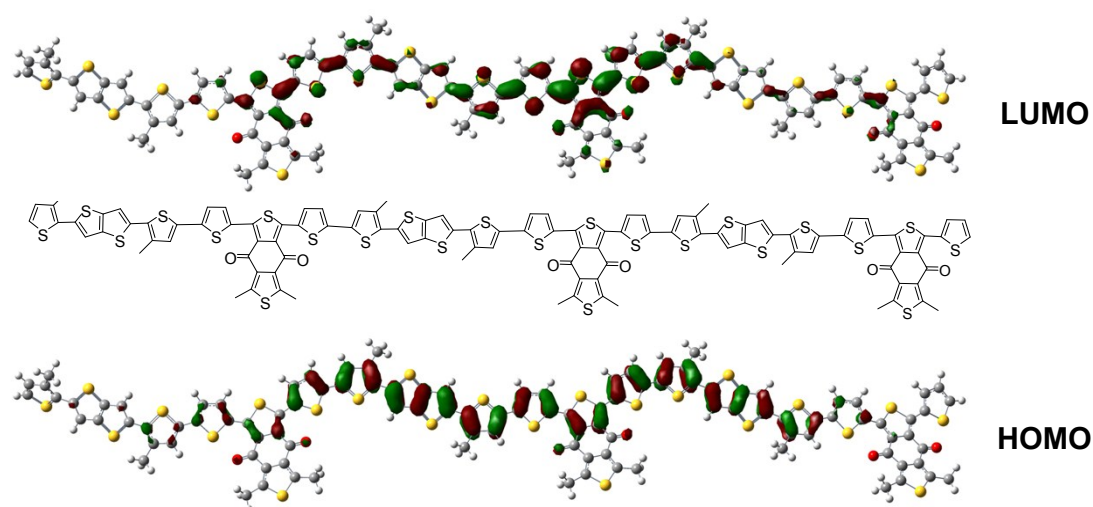


Figure S1. Theory calculated HOMO and LUMO wave functions of the geometry optimized structures for PtDDA by the DFT calculation at B3LYP/6-31G level (Alkyl chains were replaced by methyl groups to simplify calculations).

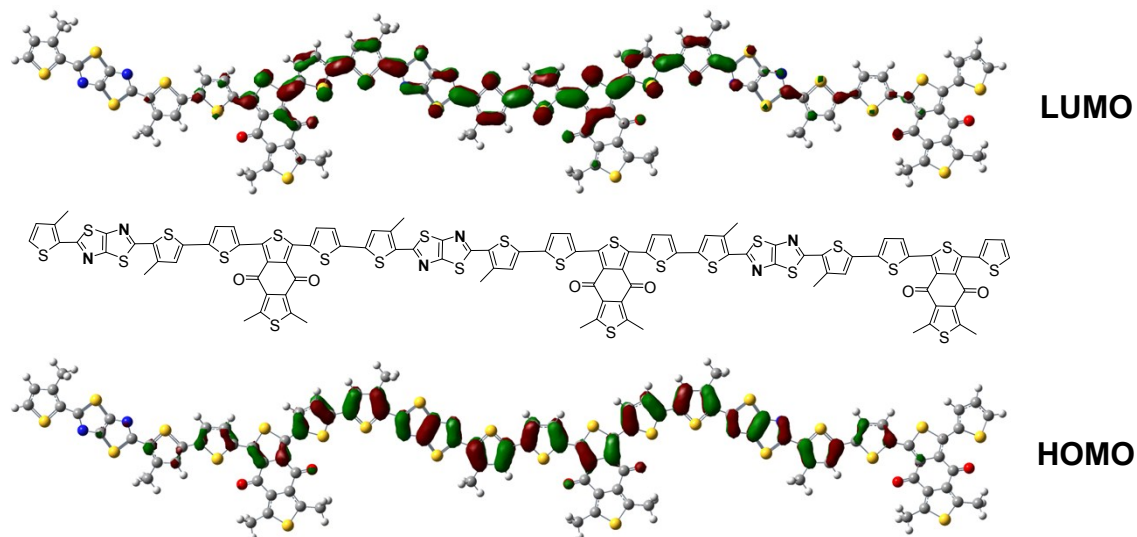


Figure S2. Theory calculated HOMO and LUMO wave functions of the geometry optimized structures for PtDAA by the DFT calculation at B3LYP/6-31G level (Alkyl chains were replaced by methyl groups to simplify calculations).

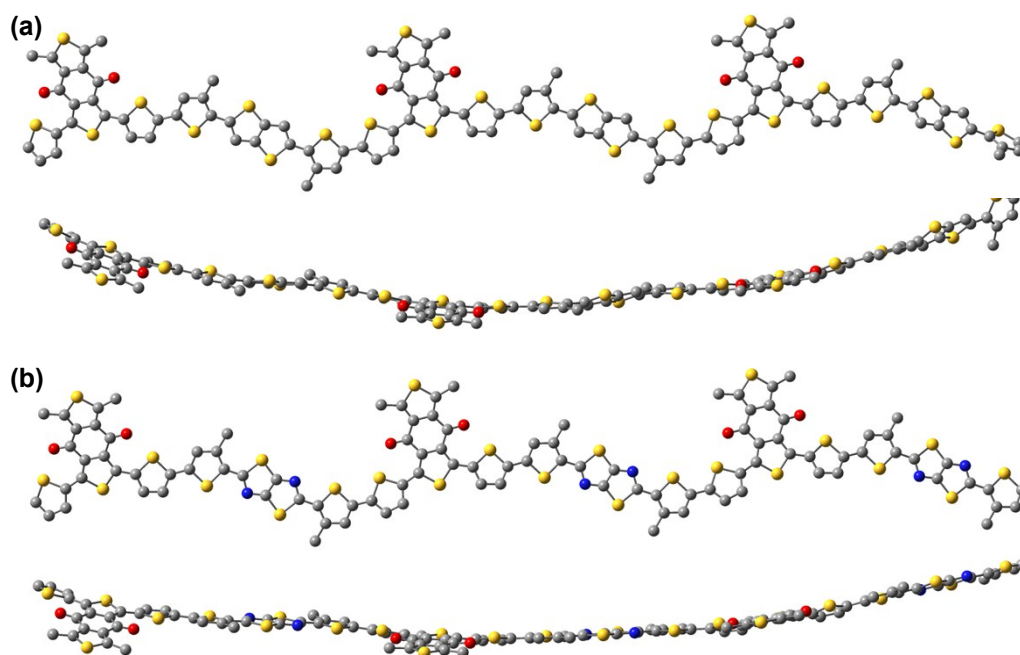


Figure S3. (a) Side view (top) and top view (down) of optimized molecular geometries of PtDDA; (b) Side view (top) and top view (down) of optimized molecular geometries of PtDAA.

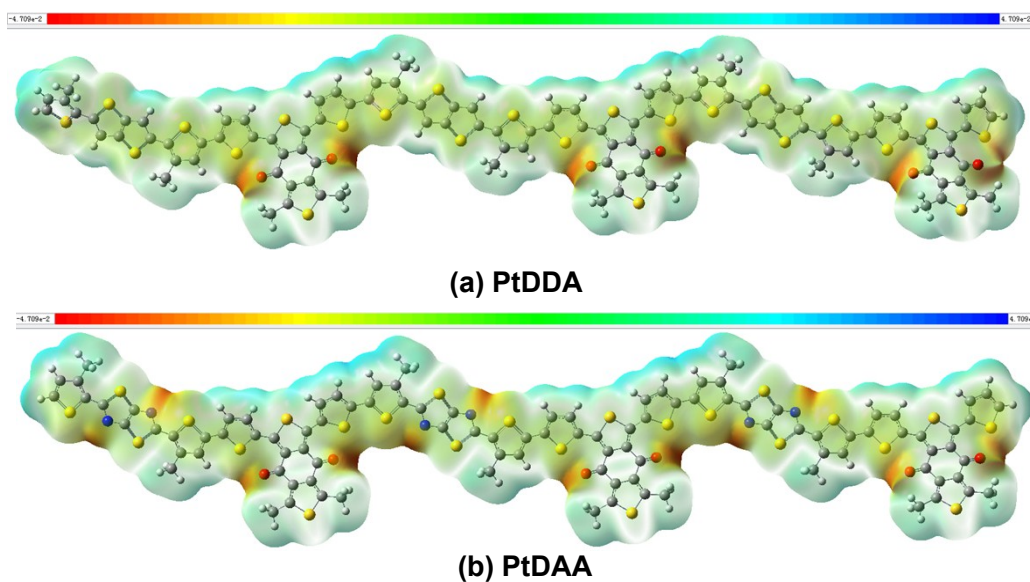


Figure S4. Map of the DFT electrostatic potential (ESP) surfaces for (a) PtDDA and (b) PtDAA. The blue color indicates positive charge, while red and yellow colors indicate negative charges.

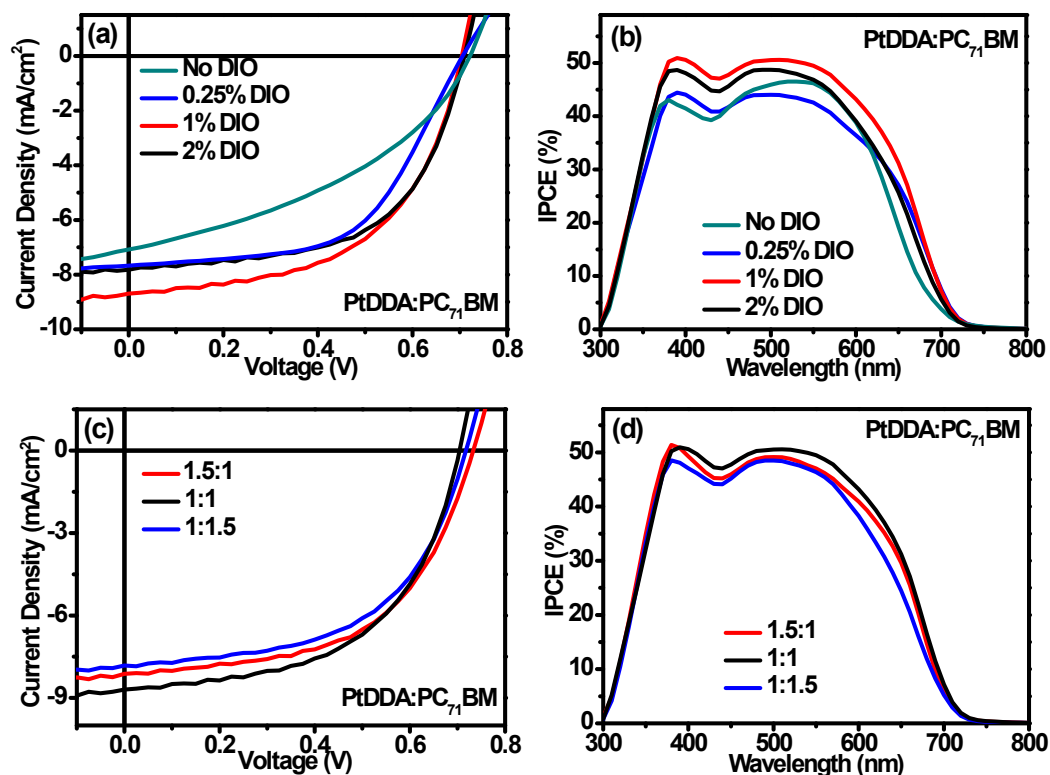


Figure S5. J - V curves of PSCs with PtDDA:PC₇₁BM active layer (a,c) and corresponding IPCE curves (b,d) in different concentration of DIO (a,b) and different blend ratios (c,d).

Table S1. Photovoltaic parameters of PSCs with PtDDA:PC₇₁BM active layer in different concentration of DIO and different blend ratios.

Ratio of D:A	DIO (%)	V_{oc} (V)	J_{sc}^a (mA/cm ²)	FF	PCE (%)
1:1	0	0.72	7.18 (7.16)	0.40	2.0
1:1	0.25	0.71	7.67(7.35)	0.56	3.0
1:1	1	0.70	8.69 (8.36)	0.55	3.4
1:1	2	0.71	7.82 (7.8)	0.58	3.2
1.5:1	0	0.733	8.12 (8.08)	0.55	3.3
1:1	0	0.704	8.69 (8.45)	0.55	3.4
1:1.5	0	0.718	7.82 (7.66)	0.55	3.1

a) The calculated J_{sc} values from IPCE spectra are shown in brackets.

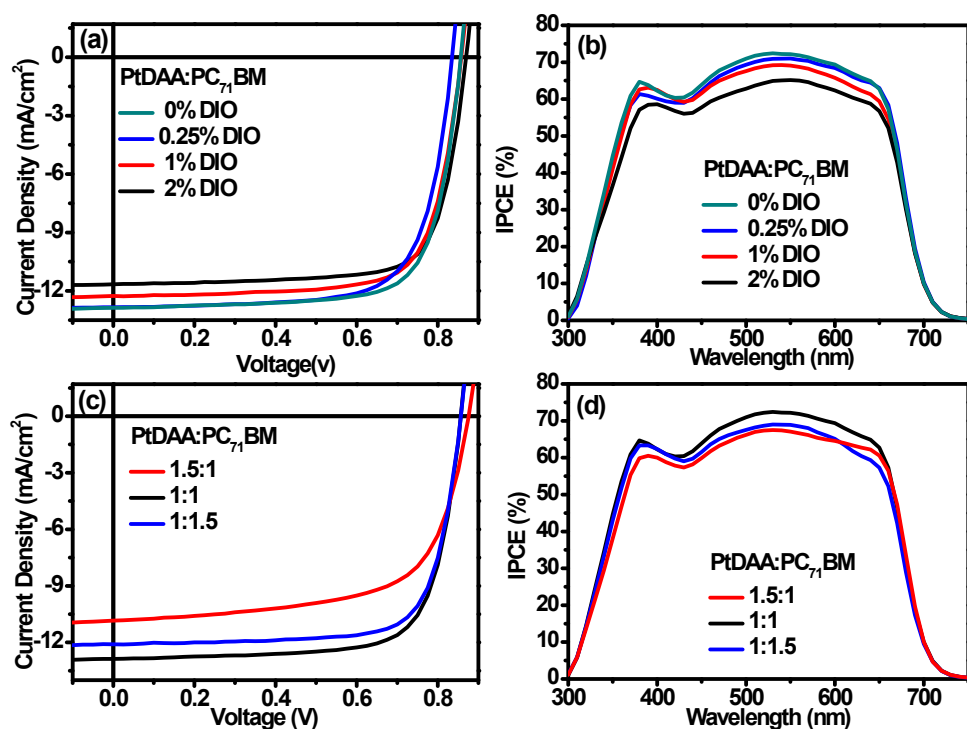


Figure S6. J - V curves of PSCs with PtDAA:PC₇₁BM active layer (a,c) and corresponding IPCE curves (b,d) in different concentration of DIO (a,b) and different blend ratios (c,d).

Table S2. Photovoltaic parameters of PSCs with PtDAA:PC₇₁BM active layer in different concentration of DIO and different blend ratios.

Ratio of D:A	DIO (%)	V_{oc} (V)	J_{sc}^a (mA/cm ²)	FF	PCE (%)
1:1	0	0.86	12.87 (12.72)	0.74	8.1
1:1	0.25	0.84	12.84 (12.55)	0.72	7.7
1:1	1	0.86	12.25 (12.19)	0.74	7.7
1:1	2	0.87	11.66 (11.51)	0.75	7.6
1.5:1	0	0.88	12.04 (12.02)	0.65	6.8
1:1	0	0.86	12.87 (12.72)	0.74	8.1
1:1.5	0	0.86	12.10 (12.06)	0.75	7.7

a) The calculated J_{sc} values from IPCE spectra are shown in brackets.

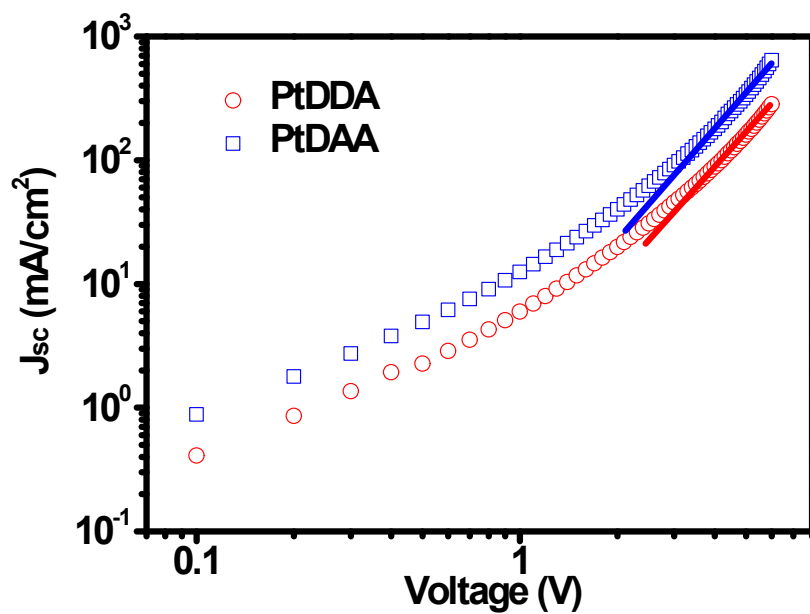


Figure S7. Current density-voltage (J-V) characteristics and space-charge-limited current (SCLC) fittings of the hole-only diodes based on terpolymers. Hole mobilities are $0.77 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and $3.44 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for PtDDA and PtDAA, respectively.

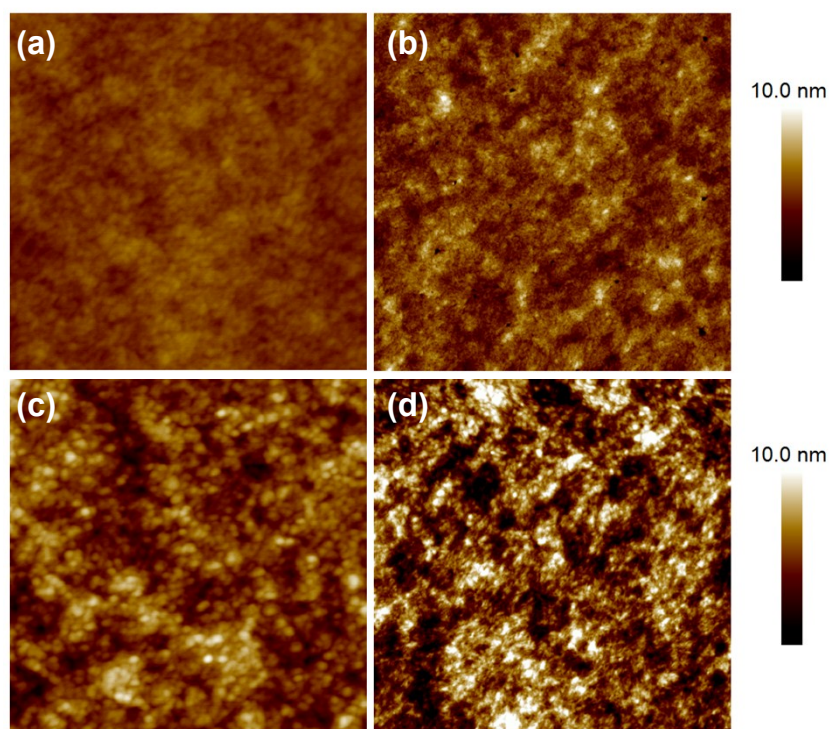


Figure S8. AFM topography of PtDDA:PC₇₁BM (a,b) and PtDAA:PC₇₁BM (c,d) BHJ layers processed without (a,c) and with 1% DIO (b,d). The scan size is 2 μm $\times$ 2 μm . The root-mean-square (RMS) roughness of a-d is 0.45 nm, 1.01 nm, 1.21 nm and 2.13 nm, successively.